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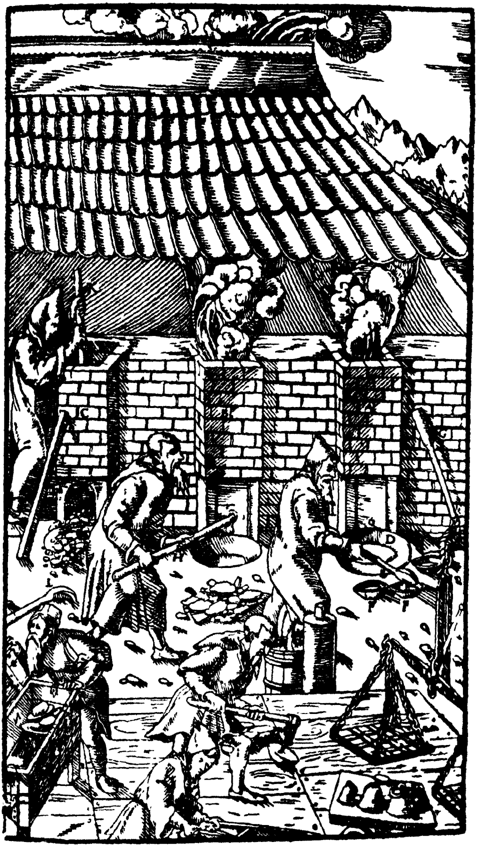

Taken from "De re metallica." *G. Agricola* 1556.

LEAD SMELTING

Three furnaces are shown. That on the left has been blown out and is being cleared of accretions; the middle one is being tapped; the right-hand furnace has been tapped, and the metal in the forehearth D is being ladled into moulds, F. The figure in the foreground is carrying a cake of metal to the scales to be weighed.

Frontispiece

PITMAN'S COMMON COMMODITIES
AND INDUSTRIES

LEAD

INCLUDING LEAD PIGMENTS AND THE DESILVERISATION OF LEAD

BY

J. A. SMYTHE, Ph.D., D.Sc.

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UNIVERSITY OF DURHAM, NEWCASTLE-ON-TYNE

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OTHERS IN PREPARATION

PREFACE

My aim in writing this book on Lead has been to present a straightforward account of the subject, free from technicalities and setting forth in outline the various processes used from the time the ore is dug out of the earth until the pure metal, and the valuable pigments derived from it, are put on the market.

I have assumed throughout that the reader has very little knowledge of chemistry and physics. Should he be totally lacking in this equipment, he will still be able to follow the story in a connected manner ; if his knowledge of these sciences is slender, he may be urged by the reading of this book to extend it.

The actual smelting of lead ore, the purification of the crude metal, and the conversion of the pure metal into Red Lead and White Lead naturally form the chief theme. The development of blast-roasting of ores and blast-furnace methods of smelting has been considerable in recent years, and the practical importance of these methods is perhaps greater than the space devoted to their description would lead one to assume.

Stress has been laid throughout on the association of silver with lead ores, since the recovery of silver from lead has always been a most important industry ; indeed, at the present day, lead-smelting is often undertaken more for the purpose of extracting silver from ores than of producing lead itself.

From the historical point of view lead has many claims to consideration for it is one of the metals longest known to mankind, and the study of the changes it undergoes on calcination has been of fundamental importance in raising chemistry to the rank of a science. For these reasons, prominence has been given to matters of historical interest connected with the metal.

Finally, lead enters intimately into our daily life. It forms the vehicle of our water-supply; it bulks largely in the paints wherewith we protect and adorn our houses; it is indispensable in printing; its use in warfare needs no comment. This phase of the subject appeals to all and accordingly I have sought to indicate the practical uses of the bodies dealt with and to emphasize what might be termed the human aspect of the subject.

My thanks for kind permission to use blocks are due to Messrs. Chas. Griffin & Co.; Messrs. Macmillan & Co.; Mining Magazine; and Messrs. Cookson & Co.

J. A. SMYTHE.

NEWCASTLE-ON-TYNE, 1920.

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LEAD

CHAPTER I

HISTORY OF LEAD

" LEAD is an imperfect metal, soft, livid, ponderous, not sustaining the fire long, infecting the hands of those that handle it with blackness, generated of much crude mercury, and impure and foetid sulphur, and comes nearest unto gold in weight and gravity."

This description of lead, quoted from the standard work of Webster on the metals (1671) is a quaint medley of correct facts and rejected theories; and it may be of interest, before narrating the story of the part played by lead in modern life and industry, to consider in brief what the ancients knew of the metal, and what theoretical ideas have arisen at different times and been supplanted or amended in the light of fuller knowledge.

Lead is one of the seven metals known to antiquity. Though it is impossible to fix a date to its discovery, there is little doubt that it was known before written records existed, or, at any rate, prior to any which have survived. It is mentioned in Homer and in the earliest books of the Bible. It formed part of the booty taken from the Midianites. " Only the gold and the silver, the brass, the iron, the tin and the lead, everything that may abide the fire, ye shall make it go through the fire, and it shall be clean "(Numbers xxxi, 22). It is probable that the metal was known fourteen or fifteen centuries before the Christian era.

In the days of the predominance of Greece, lead ore was largely mined and smelted at Laurium and the silver which accompanied the lead was separated by the process of cupellation. References to these operations and to the production of lead compounds from the metal are frequently met with among the ancient Greek writers. Later, at the time of the great Roman Empire, information on the subject became more detailed, and the elder Pliny (A.D. 23–74), in his famous *Natural History*, gives an account of the metal which, even a few centuries ago, was regarded as authoritative, and at the present day is one of the chief sources of information concerning the knowledge which the ancients possessed of this metal.

After the fall of the Roman empire, scientific knowledge found a home among the Arabians, whence it passed to the monasteries of Western Europe. This period is characterised by the growth of astrology and alchemy, and there arose that mystical association of planets and metals, which exercised such great influence on the shaping and progress of chemical investigation, and has left its mark on our language in the common use of the word mercury for quicksilver, and in numerous other ways.

The facts of this association are briefly these: Seven was a sacred number to the Egyptians and Persians and to those nations who derived their culture from them ; seven planets were known (the Sun being regarded as one) and seven metals. The rest is conjecture. Possibly the planets were dedicated to the gods and then the metals were brought into the relationship. Each of the heathen deities concerned took a particular metal under his care, and each metal acquired the qualities both of the planet and the god after which it was named. Chaucer, in the *Chanouns Yemannes Tale*, gives the connection in these words—

> Sol gold is, and Luna silver we threpe;
> Mars yren, Mercurie quik-silver we clepe:
> Saturnus leed, and Jupiter is tin,
> And Venus coper, by my faderkin!

There arose, too, a symbolism, lead and Saturn being represented by the sign—♄—, variously interpreted as the scythe of Saturn (Father Time), or as a corruption of the two initial letters of the Greek word Χ*ρονος* time. Such symbols still find use in geological maps to mark the nature of mineral veins. The evil repute of Saturn among the planets was extended to lead and, it must be confessed, with some justice, for most of the derivatives of lead are very poisonous.

The ancients had a very crude idea of what constitutes a metal and a very imperfect knowledge of the nature of the changes involved in their smelting processes. The conception of a pure substance, distinguished by definite physical and chemical properties, and of an element as an unresolvable form of matter was the acquisition of a much later day. It is not surprising, therefore, that we find much confusion and many chemically irreconcilable statements in Pliny. Litharge, for example, receives different names according to slight and unimportant differences of colour, arising from different methods of production. Tin was evidently regarded as a kind of lead, for it was termed "plumbum candidum" (shining or white lead), lead itself being known as "plumbum nigrum" (black lead). The alloy of silver and lead obtained by smelting silver-bearing lead ores, now known as work lead or base bullion, was named "stannum," a word used much later to designate tin.

The alchemists developed a definite theory of metals which, with some modifications, held the field probably from the eighth to the seventeenth century and exercised a most important influence on the development of chemistry. The statement of this theory in Holinshed's Chronicles (1577) could hardly be improved and is given herewith—

" All metals receive their beginning of quicksilver and sulphur, which are as mother and father to them. And such is the purpose of Nature in their generations that she tendeth always to the procreation of gold; nevertheless, she seldom reacheth unto that her end, because of the unequal mixture and proportion of these two in the substance engendered, whereby impediment and corruption is induced, which as it is more or less doth show itself in the metal that is produced."

Thus arose the idea of the growth of metals; of metals imperfect and perfect, base and noble; of the shortening of the period necessary for perfect development of the metals by means of medicines; of the correction of composition and the purification of the base metals into gold. This was the goal of the alchemists, and vast quantities of lead and other base metals were used in the pursuit of it. The description of lead, quoted in the beginning of this chapter, as " an imperfect metal . . . . generated of much crude mercury, and impure and foetid sulphur," is obviously couched in terms of this theory.

It so happens that at the very date (1671) when this was published, and doubtless accepted as a completely satisfactory statement, a small band of chemists were busy studying the prosaic subject of calcination and were laying the solid foundations upon which modern chemistry is built.

The prime distinction between noble metals, like gold and silver, and base metals, like lead and tin, is that the former are unaffected in the fire, while the latter lose their lustre and metallic properties and fall away into a kind of ash or dross. From the resemblance of this dross to lime (calx), it was called a calx (*pl.* calces) and the process acquired the name of calcination.

It had been recognised by Geber (eighth century A.D.) that calcination of a metal was accompanied by a gain in weight, and many were the explanations offered of this phenomenon. Some ascribed it to the loss of celestial heat or to the death of the metal, on the supposed analogy that a dead animal weighs more than a living one; others to the absorption of soot from the fire or of matter from the pan in which the metal was heated. Boyle (1673) held the view that material fire-particles were absorbed during the process. Three of Boyle's contemporaries, Ray, Hooke and Mayow made important advances in the subject by recognising the function of air, and Hooke went so far as to identify the particular constituent of air, fixed by the metal and responsible for the gain in weight, with something present in salt-petre.

At this stage, unfortunately, true progress was arrested, almost for a century by the establishment of a theory that calcination and burning were processes dependent on the loss of a hypothetical fire-stuff, or phlogiston, which escaped from the metal or burning material. A metal was thus regarded as a kind of compound of the calx and phlogiston. On heating in air the phlogiston escaped, leaving the calx behind, and when the calx was heated with some material like charcoal, which regenerated the metal, the obvious explanation was that the charcoal was rich in phlogiston. It will be apparent that the gain in weight on calcination is difficult to reconcile with the supposed loss of phlogiston, and this was one of the facts which finally led to the overthrow of the theory by Lavoisier, about 1774.

The true explanation, directly proved by experiment and free of all hypothesis and assumption of intangible fire-particles or phlogiston, is so simple that one is surprised that mankind had to labour so long to attain it. When a metal like lead is heated in air, it combines with the oxygen of the air, forming the compound lead oxide, or litharge. The increase in weight is due to the weight of oxygen fixed, as it were, by the lead; the calx is the lead oxide. The process is known as oxidation and is one of the most important of chemical processes in which the base metals take part.

When the lead oxide is heated with charcoal, the oxygen is removed from the oxide; it combines with the carbon, of which the charcoal is mainly composed, to form carbon-dioxide and the metal is regenerated. This process, involving the removal of oxygen from the calx is termed de-oxidation, or more generally, reduction; it is, as it were, correlative to oxidation; and these two processes, as the sequel will show, are of vital significance in most of the operations of smelting lead ores, purification of the crude metal, and extraction of silver from the purified lead.

Thus, in very few lines, we have indicated the historical importance of lead and the chief stages in the slow progress of scientific knowledge of the metal. In the past, metallurgical practice has not always waited on chemical explanation. Practical smelters of metals have often developed methods of proved success which have received adequate explanation only at a much later date. The handicap of imperfect scientific knowledge of a chemical process is, however, very great, and even to-day methods are employed, involving the use of large quantities of lead, which are based rather on the results of a somewhat varied experience than upon exact information of the underlying principles.

CHAPTER II

LEAD ORES: THEIR METHOD OF OCCURRENCE AND MINERAL ASSOCIATES

LEAD is an element which is widely distributed in the crust of the earth, though it is but rarely and in exceptional circumstances that it occurs in the native condition. This is readily understood when one remembers the ease with which lead is oxidised, and the many possibilities for chemical action which occur when the metal comes in contact with the watery solutions so often present under natural conditions.

The chief source of lead is the mineral GALENA, a compound of lead and sulphur, Pb S, containing in the pure condition 86·6 per cent. of lead and 13·4 per cent. of sulphur. This is a heavy mineral, of specific gravity 7·5, very lustrous and of a lead-grey colour; it crystallises well in cubes and octahedrons, the crystals being often many inches in size, and has well marked cleavage, breaking under the hammer into multitudes of cubes—from which circumstance it is frequently called Dice Ore. When heated, out of contact with air, at a strong red heat (in the neighbourhood of 1000°C.), it melts and volatilises. The molten mineral readily runs through brick-work and mixes with sulphides of other metals, such as iron and copper, forming what are known technically as *mattes*. These mattes play an important part in smelting operations. By reason of the volatility of galena, sublimates of lead sulphide are frequently found in furnaces. The changes which galena undergoes when heated with free access of air are of primary importance in roasting and smelting and will be dealt with later.

Two other lead minerals of note are the carbonate, CERUSSITE, or white lead ore, $PbCO_3$, and the sulphate, ANGLESITE, $PbSO_4$, named after the island of Anglesey. Both are derived from galena by the action of natural waters and are thus generally found in the outcrops or gossans of veins of galena. When these veins are worked from the surface, the character of the ore gradually changes, the "oxidised ores" giving place in depth to the "sulphide ores."

Though scores of other lead minerals have been discovered and described, few of them are of technical importance. Passing mention may be made of the numerous sulphide ores, most of them heavy, dark and lustrous like galena, which are compounds of lead sulphide with the sulphides of arsenic, antimony, bismuth, copper and silver; of the coloured ores, Crocoite (the chromate), Wulfenite (the molybdate), Stolzite (the tungstate), Pyromorphite (the chloro-phosphate) and Vanadinite (the chloro-vanadate); and of the chloride, Cotunnite, $PbCl_2$, found as a sublimate in volcanic districts, and the basic chlorides, like Laurionite, $PbCl_2, Pb(OH)_2$, which have sometimes, as at Laurium in Greece, been produced by the action of sea-water on ancient lead slags.

Lead ore, chiefly galena, is won and smelted in many countries. The total output of lead in the year, throughout the whole world, is well over one million tons, and four-fifths of this is produced by the United States, Spain, Germany, Mexico and Australia, the order stated being that of decreasing production. The bulk of the remainder is produced by the United Kingdom, Belgium, France, Austria, Italy, Canada and Greece. In all these countries, the mining and smelting of lead ore is, therefore, an important industry.

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Looking back to earlier times we find abundant evidence of lead mining and smelting in Greece. The silver-lead mines of Laurium are stated by Xenophon in the fourth century B.C. to have been wrought in ancient times. These mines were worked by slaves and were one of the chief sources of revenue to Athens for 300 years. The fleet which conquered the Persians at Salamis (480 B.C.) was built from the revenues of these mines. It has been calculated that they yielded two million tons of crude lead and twenty-two and a half million pounds troy of silver in the course of three hundred years. After a lapse of many centuries, the Laurium mines were re-opened in 1860 by a French company.

Spain and Britain were often extolled for their lead and silver at a somewhat later date. The mines of New Carthage (Cartagena) are said to have employed 40,000 men; those at Linares were worked in turn by the Phoenicians, Carthaginians and Romans, and some old shafts in the neighbourhood are still known as Pozos de Anibal (Hannibal's Wells). According to Pliny, Britain was a specially favoured country, for the ore was found near the surface of the earth and " in such abundance that a law was made prohibiting anyone from working more than a certain quantity of it."

It is well known that the Romans raised a great deal of lead in England. Numerous pigs of lead, some marked EX ARG. (that is, desilverised), have been found in the mining districts of Derbyshire, Yorkshire, and Shropshire, etc., and also along the great trade routes; these usually bear the name of the reigning Emperor and are remarkably like the modern pigs in marking, size, shape, and weight. Professor Phillips has very plausibly suggested that the great wall of Hadrian was built, partly at any rate, with a view to enclosing and protecting the lead mines of Northumberland and Cumberland.

The mining of lead in Britain has undergone many vicissitudes. The high-water mark of production was reached in the year 1856, when the output of dressed lead ore (76 per cent.) was 101,997 tons, from which there were extracted 73,129 tons of lead and 614,188 ounces of silver. There were then 353 mines working. In the Yorkshire mines at that time over 3,000 men were employed; at the end of the century the number was only 25. The production of lead in Cornwall and Devon from 1848 to 1884 was 63,600 tons, average about 1,800 tons a year; in the year 1917 it was 2 tons. In Cardiganshire, only 9 mines are now being worked out of over 260 that have been in operation during the last century; in Derbyshire, only 10 out of about 200 which were worked fifty years ago. Importations of foreign ore, speculation, dumping, excessive internal railway rates, conflict with sporting interests are among the factors which have been held responsible for the decay of the industry.

At the present day, the value of the lead ore raised in the British Isles is only about 0·6 per cent. of that of all the ores of the metals. The following statistics for the year 1917 exhibit the contributions made by the various counties. The total value at the mines of the lead ore raised during this year was £285,988; the total value of minerals (including coal) at the mines and quarries was £223,963,986. (Home Office Report on Mines and Quarries for 1917.)

This quantity is by no means sufficient to supply home needs, and accordingly we find that in the same year a large amount came into the country from outside sources, the imports being 8,657 tons of ore and 147,124 tons of metal, in the form of pig lead and sheet lead. Most of the foreign ore was re-exported, along with about one-fifth of the home-produced metal and over 7,000 tons of lead manufactures (white lead, red lead, etc.), and it is estimated that 149,642 tons of lead, or about thirteen times the quantity raised in the country, was available for home consumption.

Production of Lead Ore, Lead and Silver in the British Isles

	Dressed Lead Ore. *Tons.*	Metallic Lead from the Ore. *Tons.*	Silver from the Lead. *Ozs.*
ENGLAND—			
Cornwall	7·	2	—
Cumberland	720·5	513	6,445
Derbyshire	3,585	2,484	—
Durham	3,840	2,729	17,133
Northumberland	429	321	2,054
Salop	15	11	—
Westmorland	683	531	6,671
Yorkshire	42·5	33	34
	9,322 tons	6,624 tons	32,337 ozs.
WALES—			
Anglesey	—	5	—
Cardigan	896	680	7,986
Carmarthen	47	36	235
Carnarvon	141	107	2,624
Denbigh	9	7	—
Flint	824	641	5,449
Montgomery	35	66	260
	2,002 tons	1,542 tons	16,554 ozs.
SCOTLAND—			
Dumfriesshire	2,056	1,582	11,308
Lanarkshire	1,773	1,373	5,319
	3,829 tons	2,955 tons	16,627 ozs.
IRELAND—			
Sligo	4	3	52
ISLE OF MAN	165	126	7,524
Totals	15,322 tons	11,250 tons	73,094 ozs.

It would lead too far to describe even a few of the modern mines and lead-mining countries, but passing mention may be made of the great mines at Broken Hill, New South Wales, as these are the greatest lead producers in the British Empire. The first discovery of minerals in the district was in 1884, when Cerargyrite, an ore of silver was found. The town of Broken Hill was founded in 1886 and the mining of lead, silver and zinc was developed with great rapidity. The main lode is nearly 1½ miles long and averages 59 feet in breadth. It is worked by several companies and altogether about 9,500 men are employed. The yearly output is 27 per cent. of the world's total and the value of the metals raised in the 25 years from 1885 to 1910 is estimated at no less than sixty million pounds sterling. One company alone, the Broken Hill Associated Smelters Proprietary Company, produced 290,000 tons of lead and nearly five million pounds of silver between the years 1889 and 1896.

Lead ore suitable for winning occurs in some places in the form of granules scattered through the country rock which may be limestone, as in Missouri, or sandstone, as at Mechernich in Germany. The lead-bearing portion of the rock in such cases in essentially horizontal and, in Missouri, varies from 5 to 100 ft. thick, from 25 to 500 ft. wide, and almost 2 miles in length. It is not very clearly defined and its limits for practical purposes are dependent on the richness of the ore-body and the costs of working it. In England, a somewhat similar method of occurrence of lead ore, though on a small scale, is that of Cannock Chase. In most cases, however, the ore is found in mineral veins, vertical or inclined at a high angle, which are often traceable for miles and are at times worked at great depth (2,010 ft. at Foxdale, Isle of Man; 2,134 ft. at Freiberg, and 3,000 ft.

at Eureka, Nevada). These veins are in the nature of fissures in the earth's crust, often accompanied by displacement of the beds (faulting), and they are filled with minerals, spars and ores, often accompanied by fragments of the country rock from the adjacent strata.

In any particular mining district, the direction of a system of veins is more or less constant. In Derbyshire, for example, they run mostly in two directions, W.–E. and N.W.–S.E.; in Lanarkshire, N.W.–S.E. and W.N.W. –E.S.E. In the mining district of Alston Moor, on the borders of Cumberland and Northumberland, the veins which run W.–E. are termed "right running" and are usually productive, while those which run N.–S. are termed "cross" veins and are generally barren; they belong to an earlier age of formation. Ore is often abundant where veins intersect and cross veins frequently carry ore for some distance from their meeting with right running veins. The flats or horizontal offshoots of veins are also highly productive, especially when these are situated in the Great Limestone—one of the most important limestones in this region.

The system of veins in the district around Leadhills and Wanlockhead is shown in the accompanying map. (Fig. 1.) (*See* J. Mitchell, *Min. Mag.*, July, 1919, p. 15.)

The contents of mineral veins are very varied. Sometimes a mass of solid ore is met with, but more generally in workable veins the ore is mixed with country rock (rider) and crystallised minerals—the vein-stuff or gangue of the miner. The nature of these differs according to locality and depth. Fluorspar (CaF_2) is common in Weardale and Derbyshire; in the latter county this mineral gives place in depth to Heavy Spar or Barytes ($BaSO_4$), and the same change is sometimes noted as a vein is worked across country. Calcite or calcspar ($CaCO_3$) and Quartz (SiO_2) are frequently

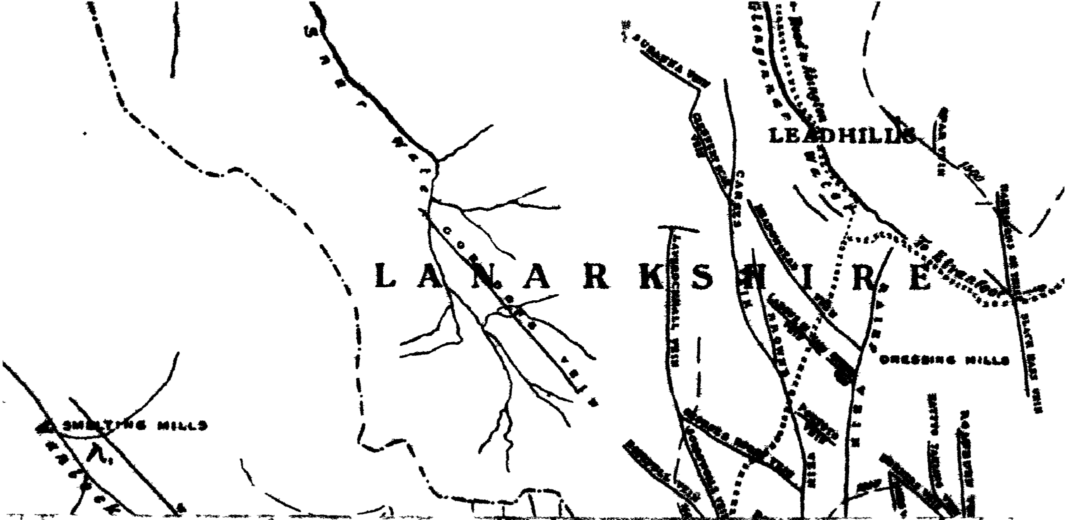

Fig. I

Map of district about Leadhills (Lanarkshire) and Wanlockhead (Dumfriesshire), showing the position of veins of lead ore. The veins are marked by black lines; the various streams flow to the Clyde and Nith; shafts are marked by small circles.

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met with in veins, the former especially when the adjacent rock is limestone, the latter where it is quartz. Iron pyrites ($Fe S_2$), ores of copper like Chalcopyrite ($Cu FeS_2$) and Zinc Blende ($Zn S$) are frequent associates of galena. Sometimes the lead and zinc sulphides are intimately mixed and separation becomes a difficult matter. Galena is often replaced by blende in depth. Altogether, the association of lead and zinc is noteworthy, and the two are often produced from the same mine, as is the case at Broken Hill. It may be noted that the intimate mixture of the two ores is almost useless for smelting.

The frequent association of silver with lead is a fact worthy of special notice. It is reckoned that two-thirds of the world's silver production is derived from argentiferous galena. A rough average of the ratio of silver to lead in galena is 1 to 5,000, but it must be understood that there is great individual variation, some lead ores passing into silver ores, others, as in the great Missouri belt, being practically free from silver. The silver content of lead is usually stated in ounces per ton, and the mean values over a number of years for several British mines are: Cumberland, 8 ozs.; Yorkshire, 7 ozs.; Devonshire, 23 ozs., and Cornwall, 63 ozs. per ton. The silver is usually accompanied by a small amount of gold, of the order of 1 per cent. of the silver, and both precious metals pass into the lead during smelting and are recovered thereform by the desilverising process. A " mine royal " is one in which the value of the precious metals in the lead produced from it exceeds the costs of extraction; otherwise, it is a poor mine. Ancient grants of mines paying tribute to the King often specify " mines of lead holding gold and silver," and the Church, the lord of the soil, and the curate of the place sometimes figure as beneficiaries

CHAPTER III

THE FINDING AND MINING OF LEAD ORE AND THE PREPARATION OF THE ORE FOR SMELTING

THE old authors were fond of speculating on the discovery of the metals, and one favoured account ascribes this to the burning of forests which grew on mineral deposits. The Latin poet Lucretius (99–55 B.C.) describes this in a passage of his great work *De rerum natura*, of which the following is a somewhat free translation by Creech—

Pow'rful gold first raised his head
And brass, and silver, and ignoble lead,
When shady woods, on lofty mountains grown,
Felt scorching fires; whether from thunder thrown
Or else by man's design the flame arose.
Whatever 'twas that gave these flames their birth,
Which burn'd the towering trees and scorched the earth,
Hot streams of silver, gold, and lead and brass,
As Nature gave a hollow proper place,
Descended down and formed a glitt'ring mass.

Though it is possible that metals have been discovered in this romantic manner, and, indeed, there is a record of such a happening in Croatia as recently as the year 1761, it is more likely that the prosaic method of testing in the fire stones or minerals, distinguished by their weight, lustre or other striking properties, led primitive man to the knowledge of the metals. It is noteworthy that the seven metals anciently known all occur either in the native condition, or as ores easily reducible to metal at a comparatively low temperature.

Many valuable deposits of lead and silver ores have been discovered by accident. The famous mines at

Freiberg are stated to have been discovered by a flood which laid bare a vein of the ore, and there is a tradition that in the year A.D. 936 a horse named Ramelus, by pawing on the ground, disclosed a hidden vein and thereby achieved immortality, the town of Rammelsberg being named after him.

The divining rod has often been resorted to, in bygone days, and adepts in the art were very particular in the choice of suitable material for their purpose. Thus a rod of pitch pine was selected in the search for lead and tin, ash for copper, and hazel for silver. There are probably many people, even to-day, who pin their faith on the indications given by the divining rod.

The modern prospector for metals must adopt very different methods if he hopes for success. He is careful to follow up indications of ore and spar in the pebbles of streams, until the position of the vein or deposit has been approximately fixed. Trenches cut in different directions will then frequently expose the ore.

A method of cutting channels by water, known as hushing, was frequently employed in this country up to quite recent times. Water was collected on a hillside by means of a dam and a shallow trench was cut downhill. On opening the dam, the water flowed out with considerable force down the trench, removing the peat and surface deposits, exposing the rock beneath and, if fortune was favourable, the veins of ore which traversed it.

The geological structure of the country affords most valuable clues in the search for ores, and indications are also obtained from the colour and contour of the ground, the vegetation, the early or late melting of hoar-frost in the morning, and the character of springs and the deposits from them. As the saying goes : " Every lode has its own water," and from the nature of this the discerning person can often draw important conclusions as to the neighbourhood of minerals.

The outcrop of a vein is generally weathered and may contain secondary minerals, formed by atmospheric agencies from the original minerals. Oftentimes it is rich in iron ores, and the presence of a good "iron hat," as it is termed, is usually regarded by miners as a favourable indication of a rich lode.

When a miner has discovered ore and wishes to mine it, he experiences but little difficulty in establishing his claim and beginning operations. Mining laws in general seem devised in order to help the miner, provided that he makes a real and continuous effort to raise ore. In Derbyshire they were administered by a Bar-master, "an indifferent person betwixt the lord of the field, or farmer, and the miners," chosen by the miners and merchants, and there was an organisation of miners' courts with juries of twenty-four miners for the trial of cases.

According to these ancient laws, it is lawful "to dig, delve, subvert, mine and turn up all manner of grounds, lands, meadows, closes, pastures, mow or marshes for lead ore, of whose inheritance soever it is,—dwelling houses, highways orchards or gardens excepted."

A miner, having found a vein, applied to the Bar-master for leave to work it; the Bar-master attended to receive the first dish of ore and then made a grant of a meer, or 29 yards, to the miner and the adjoining half-meer was taken for the king. The condition imposed was that of continuous working, an intermission of three weeks depriving the miner of his rights. Legal possession of a mine was indicated by the erection of stows for drawing ore; this condition was relaxed at a later date and only a model, "in sight of all men," was required.

Penalties for misdemeanour were numerous and somewhat severe from a modern point of view. It was the duty of the Bar-master to collect fines and to punish non-payment of these by the stocks, where the delinquent had to sit "twelve hours pining, with a paper on his back showing for what offence he sits there." A fine of 5s. 4d. was imposed for shedding blood, and also for underground trespass; whistling (which was held to frighten away the ore) was punished by chastisement, and detention in the stocks awaited "such persons as swear, curse, or commit any other misdemeanours in the mine."

These brief extracts will afford some idea of the quaint mining laws which have been operative in Derbyshire from time immemorial, and are even to-day by no means extinct. In other parts of the country, mining affairs were managed in a simpler way. In the famous lead-raising district of Alston Moor, for example, a miner who wishes to try a promising vein makes application to the agents and is usually granted permission to work for six months, on the conditions that he shall make trial within one month of the grant, continue regularly until the end of the term, and employ at least two pickmen. Of the ore raised, one-fifth is to be paid as duty or rent. If the venture prospers, a general grant of a parcel of land may be obtained from the manor.

To mine the ore, a shaft is sunk or a level driven along a suitable bed, the floor of the level rising gently in order to drain off water. From the level, the vein is reached by rises or sumps, that is, shafts driven upwards or downwards. The vein is then divided into allotments of 15–20 fathoms, and each is worked by partnerships of men who bargain with the master to work for a certain period at a certain price, inclusive of labour, candles, powder, conveyance of ore to the day and washing of ore.

The ore as raised from the mine requires a more or less elaborate treatment before it can be delivered to the smelter. The vein-stuff or gangue with which it is mixed must be removed and a " concentrate " of the valuable ore obtained. For this purpose, the bouse, or mixed ore and gangue, is delivered on to a revolving table, picked over by hand and roughly sorted into good ore, mixed material and deads, or worthless stuff. The bigger lumps are broken and again picked, and the combined mixed material is then treated on the washing floors. Here, by continuous crushing and passing through screens, the material is sorted into grades, according to size, and each grade is then submitted to agitation in water, by means of jigs, concentration tables, etc., by which the lighter, earthy and sparry particles are washed away and the heavier minerals assembled in a concentrate. For a description of the process employed the reader is referred to Chapter II of Mr. Pickard's book on Copper in this series. Here it will suffice to say that the difference in specific gravity of the various minerals and rocks is utilised in order to bring about separation, the broken material being kept in constant agitation in a stream of water, so that the lighter particles rise and are swept away, the heavier sink and are gathered apart.

The following table contains the specific gravities of the chief lead ores and the minerals usually associated with them, and it will be noted that galena is specifically much heavier than its common associates. It should be mentioned too that limestone has substantially the specific gravity of calcite and sandstone of quartz, the mineral and rock in each case being practically identical in chemical composition.

Specific Gravity of Ores and Minerals.

Lead Ores—Galena, 7·5.
Cerussite, 6·6.
Anglesite, 6·3.
Copper Ore—Chalcopyrite, 4·2.
Zinc Blende, 4·1.
Iron Pyrites, 5·0.
Heavy Spar or Barytes, 4·6.
Fluorspar, 3·2.
Calcite or Calcspar, 2·7.
Quartz or Rock Crystal, 2·6.

Having followed the various stages whereby a concentrate of the chief lead ore, galena, is obtained, we shall now turn our attention to the chemical changes involved in the extraction of lead from the ore, and the methods of smelting whereby these changes are successfully effected.

CHAPTER IV

THE CHEMICAL CHANGES INVOLVED IN SMELTING

THE oxidation of lead when heated in air, and the reduction of lead oxide when heated with carbon, are two of the simplest of chemical changes and are of fundamental importance in the smelting and refining of lead. The extraction of lead from galena requires the intervention of other chemical reactions which need some consideration. The problem is to find some means of removing the sulphur, or desulphurising the ore, and the simplest way to achieve this is to heat it with iron. Sulphide of iron is produced and lead is set free, as expressed by the chemical equation

$$PbS + Fe = FeS + Pb.$$

This method can be used, and, indeed, has been used in the past, but it labours under certain difficulties which have militated against its development.

When galena is roasted, *i.e.*, heated with free access of air, the sulphur is burnt to form the gas, sulphur dioxide, and the lead is oxidised to litharge. If the reaction were to stop at this point, it would be a simple matter to reduce the litharge with carbon and obtain the metal in this way. It happens, however, that the sulphur dioxide (SO_2) itself becomes in part oxidised to sulphur trioxide (SO_3), and as the litharge is a strongly basic oxide and the sulphur trioxide a strongly acidic oxide, the two unite and form a salt, lead sulphate, $PbSO_4$, in much the same manner as an acid and an alkali neutralise one another. As in the roasting process, some of the sulphur dioxide escapes before it can be converted into the trioxide, the ordinary effect of roasting is to convert galena into a mixture of lead oxide (PbO) and lead sulphate ($PbSO_4$).

Now, when lead sulphide is mixed with lead oxide or lead sulphate and strongly heated, mutual reaction between the sulphide and the oxidised compounds takes place in such a manner that, when the correct proportions are present, all the sulphur and oxygen are eliminated as sulphur dioxide and only the lead remains. This is illustrated by the two equations—

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

The practical application of these reactions is obvious. Galena is roasted in such a manner that it is partly oxidised to oxide and sulphate of lead ; at a certain stage the air supply is cut off and the temperature raised, when the unaltered galena reacts with the oxidised compounds yielding the metal. As these reactions are carried out by the agency of air (*i.e.*, atmospheric oxygen), the process is called the "air-reduction" process. To utilise this method successfully a rich ore or concentrate of galena is requisite, containing, say, 75 per cent. of lead.

If the ore contains much silica (SiO_2) in the form of quartz or sandstone, this silica, being an acidic oxide like sulphur trioxide, unites with lead oxide, producing a slag of lead silicate, in which the lead is chemically locked up as effectually as it is in galena. From the lead silicate the metal cannot be liberated by the reducing action of carbon. It is liberated, however, by the action of metallic iron, silicate of iron being formed; and if other basic oxides like lime (CaO) and ferrous oxide (FeO) are present in the charge, the silica combines with these, forming a slag of calcium and iron silicates, and the lead oxide is then free to react with carbon or lead sulphide, thereby yielding up its lead in the metallic condition.

Poorer ores containing much gangue are thus blended with fluxes, like lime and oxide of iron, the proportions of the constituents being selected so that when the mixture is heated with the necessary fuel, the earthy and silicious materials unite to form a slag of calcium and iron silicates, and metallic lead is set free, the combustion of the fuel affording the temperature necessary to melt both slag and metal. The separation of these in the molten condition is then a simple matter owing to the great difference in their relative densities.

The smelting of lead ores in the blast furnace depends on these reactions. It only remains to be stated that owing to variations in the composition of furnace charges and in the conditions existing in smelting furnaces, the chemical reactions characteristic of one process may enter to a greater or less extent into the other process.

Lead ores, no matter how carefully dressed, always contain certain amounts of metallic impurities, from which the metals are liberated during smelting. These impurities pass wholly, or in part, into the lead and affect the properties of the metal, usually rendering it hard. The crude lead produced by smelting contains variable amounts of these impurities, chief among which are arsenic, antimony, bismuth, tin, copper and zinc, and the precious metals, gold and silver—if by a stretch of imagination these can be termed impurities. This is known as "work lead" or "base bullion." To befit the lead for industrial uses, and to make possible the extraction of the precious metals, the crude lead must undergo a process of purification, which can be carried out without the loss of silver (and gold). The purified lead-silver alloy is then desilverised, and the desilverised lead, now of a high degree of purity, is soft and suitable for the manufacture of pipes and sheets, and for conversion into such compounds as white lead and red lead, and generally for all industrial purposes.

CHAPTER V

SMELTING IN THE ORE-HEARTH

THE ancient methods of smelting lead ores were of the simplest description. A fire-place built of stones, with suitable openings for the admission of air, was set up on an exposed hill-side in a position where advantage could be taken of the prevailing winds. A fire of wood was kindled and pieces of pure ore thrown in. A certain amount (probably not great) of the ore was reduced to metal, and this was afterwards recovered from the ashes. The conditions were such that some galena would certainly become oxidised by the air, and opportunity would be afforded in other parts of the fire for those reactions of reduction to take place whereby the metal is set free. The numerous bayle-hills or boles scattered over the mining districts of the North of England mark the sites of this primitive industry.

The first step in the development of this method was to regulate the access of air to the fire by the use of a controlled, mechanically worked blast. In course of time the small furnace known as the ore-hearth or Scotch hearth was produced, and this has been extensively used in Britain for two or three centuries.

Smelting in the Ore-Hearth. This furnace consists of a rectangular, cast-iron pan, 31 ins. long, 24 ins. broad (from front to back) and 12 ins. deep, capable of holding about 30 cwt. of lead. A ledge runs round the two sides and back. On the front is cast the work-stone, a sloping plate of iron, with a fall of 4 ins., surrounded by a rim or ledge 1½ ins. high and having a groove down which molten lead runs from the pan to the melting pot, the latter serving as a receptacle for the metal. The blast enters through a pipe at the back of the furnace. The nozzle of this rests on a plate of iron called the backstone, at a height of about 6 ins. above the pan, and fits into a hole in another plate called the pipestone, which rests on the backstone and is about 8 ins. high. These two " stones " run the length of the furnace and form a backing to it, 31 ins. long and 14 ins. high. The pan is set in brickwork and is fitted with a hood to carry off fumes and connected with flues to condense the lead fume. The pan is kept full of molten lead upon which the charge floats and as fresh lead is produced it trickles into the pan and overflows thence down the groove in the workstone into the pot.

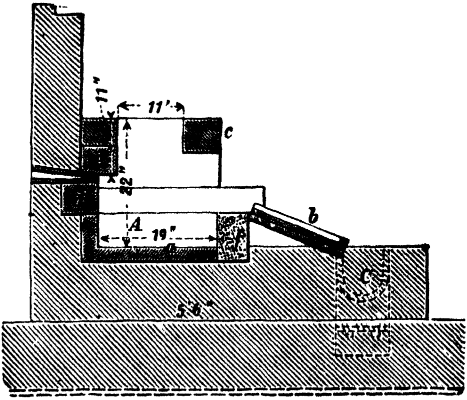


Fig. 2
THE ORE HEARTH

Fig. 2 shows the construction of the Ore Hearth. *A* is the hearth filled, during working, with molten lead ; *b*, the workstone ; *C*, the pot for the reception of the lead which overflows from the hearth down the workstone ; *d* is the backstone on which the nozzle of the blast-pipe rests ; and *e* the pipestone provided with a hole in which the nozzle fits.

In working, peat and coal are thrown on the hearth, then a charge of *bouse* or ore, and the blast is turned on. At times the charge is loosened by thrusting a poker into the lead bath and raising the mass, and a portion is brought on to the workstone, where the lumps of slag (" grey slag " it is named) are picked out and thrown aside for subsequent treatment, and the *browse*, or partly fused ore, is returned to the hearth. Fresh fuel and ore are added and care is taken, by throwing a turf in front of the blast pipe, that the blast is well distributed through the charge. If the material shows a tendency to fuse or become pasty, a little lime is added. Two men attend the furnace and produce 14 to 28 cwts. of lead in an eight-hour shift.

The chemical changes involved in this process are essentially those of air reduction; galena is oxidised to oxide and sulphate of lead, and these two compounds react with unaltered galena to produce lead and sulphur dioxide. In addition, some lead oxide is reduced by the carbon of the fuel to metallic lead. The reactions of oxidation and reduction follow one another rapidly; some parts of the charge suffering oxidation, while in other parts reduction is taking place, local conditions of composition and, to some extent, temperature determining the nature of the reaction.

The temperature maintained in the ore-hearth, though high enough to bring about the necessary chemical actions and to melt the lead, is not so high as to cause the slags to melt. The slags consist largely of oxidised compounds of lead and they require fresh treatment in order to recover the lead which they contain. They are, therefore, smelted again with carbonaceous fuel (peat, coal or coke), sometimes with the addition of iron slag, at a temperature sufficiently high to melt the whole charge.

The operation is performed in a slag hearth—a small, rectangular shaft furnace worked with a single blast-pipe or tuyere. The bottom of the furnace is a sloping plate of iron upon which is laid a bed of cinders, also sloping to the front of the furnace and reaching almost up to the blast-pipe. A peat fire is kindled and then the grey slags and coke are fed in alternately. Reduction of the slags takes place and the lead trickles through the cinders and escapes into the lead pot set in front of the furnace; but the slags, owing to their viscosity pass more slowly through the ashy filter. They are eventually run off and granulated by quenching in water, and the granulated material is afterwards washed in order that shots of metal which have been entrapped in the slags may be recovered.

By the use of these two furnaces, the ore-hearth and the slag-hearth, rich ores containing 70 per cent. and upwards of lead are readily treated, some 60 per cent. of the metal in a fairly pure condition being extracted on the ore-hearth. The lead obtained from the slag-hearth, slag lead as it is called, is not so pure as that from the ore-hearth.

The ore-hearth, though extensively used for several centuries, has not proved amenable to much improvement. Its length has been limited to about four feet and its output is low; labour is heavy and the removal of fume has been difficult, though for this purpose the furnace is set under an arch connected with flues to a high chimney. Its main advantage lies in its simplicity and cheapness, and in the rapid extraction from the ore of much of its lead, in a fairly pure state. It is a suitable furnace for remote districts where only a limited supply of high-grade ore is available

One of the most recent improvements was introduced in America at St. Louis, and is known as the St. Louis hearth, or, sometimes, after the name of its inventor, the Newnam hearth. The chief merits claimed for this are: (1) a mechanical rabble, which is worked from a carriage travelling on an overhead track. This arrangement is worked by electrical power. The rabble arm, a stout poker, loosens the charge with a motion like that of the hand rabble, being thrust into the fire at an angle downwards, levered up and withdrawn horizontally. After withdrawal, the carriage moves forward four inches and the stirring is repeated, and at the end of a trip it is run back without rabbling to the far end of the furnace and is ready for a fresh start.

(2) An effective double hood whereby the fumes are carried off to the flues and condensers and the workmen are shielded from heat. Modern methods of fume condensation (v. *postea*) are used.

It has been found possible to double the length of the hearth without increasing the hand labour, only two men being employed to attend a furnace eight feet in length. The greater length and capacity necessitate a greater air supply, and this is furnished by 16 tuyeres which are placed at equal distances apart along the back of the furnace. This furnace yields a greater percentage of lead with smaller consumption of coke breeze, which is the fuel used, than the older ore-hearth.

CHAPTER VI

SMELTING IN THE REVERBERATORY FURNACE

IN the shaft or blast furnace, the type to which the ore-and slag-hearths belong, the fuel, which by its combustion yields the heat essential for the chemical reactions of smelting to take place and itself enters into the chemical processes as a reducing agent, is mixed with the ore-charge and the necessary air is forced into the mixture by bellows or some blowing contrivance. The reverberatory furnace is very different in structure and function. The fuel is burnt alone on a grid, and the ore rests on a hearth, separated from the fire by a low wall or fire-bridge. A flue, at the end of the hearth farthest from the fire, communicates with a tall chimney which affords the draught necessary to draw air through the fire-place and the furnace chamber. The hot gases from the fire-place heat the low arched roof over the hearth, and the heat is reflected or "reverberated" therefrom on to the top of the charge. The material to be furnaced is thus heated from the top, essentially by radiation from the roof of the furnace. By manipulation of dampers, and by keeping side doors open or shut and by suitable firing, the temperature of the furnace can be altered to suit requirements, and the atmosphere within can be maintained either as an oxidising one (containing excess of air), or a reducing one (containing excess of gases from the fire), or, finally, it may be made indifferent with respect to these two conditions.

This type of furnace was invented in the seventeenth century and the stimulus to its application came from the growing scarcity of wood and the development of coal-mining, for by its use coal could be used as the source of heat, without the drawback of contaminating the ore with its ash. It seems to have been first applied in England to the smelting of tin and copper ores in Cornwall and Wales. It was introduced into Derbyshire for smelting lead ores in 1747, and in a few years completely supplanted the ore-hearth. The latter furnace is still used in Scotland and was in operation in 1918 in Weardale.

If one considers only the chemical reactions of the air-reduction process, then the reverberatory method of smelting affords the best insight into them, for the two main reactions, viz., roasting or oxidation, and smelting or reduction to metal, are distinct, both in point of time and manipulation. They may also be carried out in the same furnace and during one suite of operations. Though there are many variations of method and modifications of furnace, it will suffice for our purpose to describe what is known as the Flintshire furnace and to illustrate its use in smelting lead ore.

The Flintshire Reverberatory Furnace is shown in longitudinal section in Fig. 3. A is the fire-place separated from the hearth B by the fire-bridge which is hollowed for the purpose of cooling. The arched roof of the furnace is provided with an opening over which is the charging hopper *e*. At the end, remote from the fire, are the flues through which the gaseous products escape ; *a*, *a*, *a* are the working doors.

Fig. 4 is a horizontal section of the same furnace along the line C D. The flues are divided so as to spread the flame. The well of the furnace in which the lead is collected is placed in the coolest place, adjacent to the tapping pot *d*.

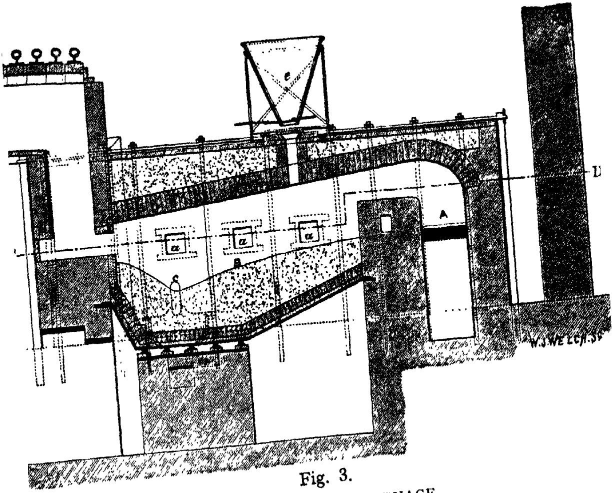


Fig. 3.
THE FLINTSHIRE FURNACE

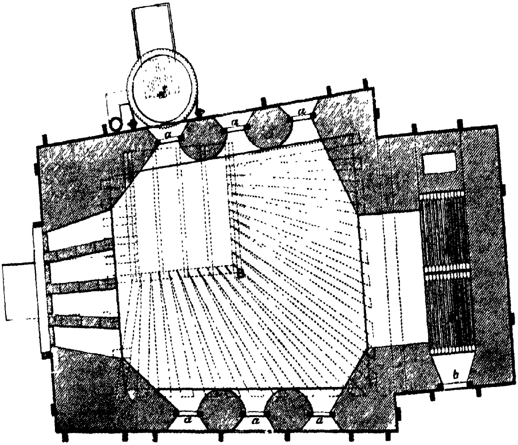


Fig. 4.
THE FLINTSHIRE FURNACE

The process is carried out in this way. A charge of 21 cwts. of finely divided ore is fed through the hopper on to the hearth, which is hot from the working of a previous charge. The ore is spread over the hearth, rabbled from time to time to expose fresh surfaces to the air, and the doors are left open and the dampers closed so as to give air free access and to keep the temperature low. It is essential that the temperature should not be high enough to melt, or even partly melt, the ore, for in that case permeation of the material by air and effective oxidation would be arrested.

After about two hours, the grate is cleared, the fire made up, the damper opened wider and some of the side doors closed. The heat is thus urged and reactions take place between unaltered sulphide and the oxidised compounds of lead produced in the first stage, with the result that lead trickles into the well and the mass effervesces owing to the escape of sulphur dioxide. In about an hour the mass melts down. The whole charge has not, however, entered into the reactions necessary to free all the lead, so that the above operations have to be repeated.

To effect this, the doors are thrown open to cool the charge, and slaked lime is thrown on the molten slag, which rests on the lead in the well. The slag becomes thickened and is then pushed back, or "set up," as it is termed, near the fire-bridge. The front working-doors are opened and oxidation proceeds for half-an-hour. After this period, the doors are again closed, the damper opened, and the fire urged, when the smelting reactions are again produced, a fresh quantity of lead trickles down and eventually the slags melt and flow into the well.

It only remains now to withdraw the slag and tap the lead. For the former purpose, the doors are thrown open and two shovelfuls of lime added and well worked with the slags. When these have thickened, they are pushed back from the tapping-hole and the lead tapped into the pot outside the furnace. The slags are then raked out and the furnace is ready for a fresh charge. The time occupied in these operations is about five hours, and about 90 per cent. of the lead in the ore is extracted.

The slags are rich in lead and are smelted again either in another reverberatory or in a blast furnace.

CHAPTER VII

SMELTING IN THE BLAST FURNACE

THE methods of smelting so far described are restricted to high-grade ores and concentrates consisting essentially of galena and freed in large measure from the gangue or vein-stuff with which the ore is usually accompanied. We have seen, however, that certain furnace products, such as the grey slags from the ore-hearth, require a different method of treatment, and an illustration in point has already been given in the description of the slag-hearth. There exist, also, other ores of lead, like the carbonate, cerussite, which by their very nature are incapable of entering into the reactions of the air-reduction process, and there are large quantities of low-grade sulphide ores which contain so much earthy and silicious materials that any attempt to smelt them by this process would be seriously hindered or even rendered impossible by the presence of so much barren matter.

In such cases, the blast furnace is used and the objects sought are to extract the lead from the charge in the metallic condition, and to provide that all the earthy and silicious materials should unite chemically to form a fusible slag, free from lead, and easily separable from the metal. To achieve this, it is necessary that the lead should be present not as sulphide, but as oxide, for the chemical conditions in a blast furnace are essentially reducing, since the ore is in intimate contact with the fuel and the charge is traversed by reducing gases (carbon monoxide). In these circumstances lead sulphide would simply melt and run through the furnace unaltered, whereas if the lead is present as oxide, this is reduced by carbon and carbon monoxide to the metal.

To understand this rightly one should realise what are the characteristics of a blast furnace and how it differs from the reverberating furnace already described. The blast furnace is essentially a shaft, into the top of which ore and fuel are fed, whilst the products of smelting, viz., metal, matte and slag are withdrawn in a molten condition near the bottom. Air requisite for combustion of the fuel is blown in through tuyeres or blast pipes near the bottom, and the hot gases traverse the charge and are drawn off through a pipe near the top. The base of the shaft contains the crucible in which the molten products of smelting are collected and from which they overflow or are removed by tapping. Just above the top of the crucible are the tuyeres, and the zone in the immediate neighbourhood of these is the zone of fusion, the heat being greatest here owing to active combustion of the fuel. Above this zone the charge remains solid and travels slowly down the shaft, becoming heated in the meanwhile and undergoing some of the chemical changes which are completed in the zone of fusion. Generally, the shaft is widened above the tuyeres, so that the velocity of the uprising gases is checked and more of their heat transferred to the descending charge.

Some of the details of construction of the blast furnaces used in lead smelting will be considered later.

It will be apparent that sulphide ores, unsuitable for smelting in the ore-hearth and reverberatory furnace, cannot be immediately treated in the blast furnace. It is essential first to remove the sulphur, that is, to convert the lead sulphide into lead oxide (or perhaps lead silicate) and this change is brought about by roasting. Accordingly, we have to consider first the methods employed in roasting the ores, and then the actual smelting of the roasted ores in the blast furnace.

Roasting of the Ores. A great many methods are available for roasting sulphide ores. One of the simplest is to lay out a bed of fine ore, say, 200 ft. long, 20 ft. broad, and 6 ins. thick, place upon this a layer of wood, and then build up a pile of ore about 6 ft. high on top, using coarse ore for the lower layers and covering with slimes or fine ore. The wood is kindled, and once the roasting is started it continues gently throughout the whole mass, the heap burning much as a gardener's smother-fire, or the waste shale from a coal-pit, the heat of oxidation serving to keep up the temperature to the requisite degree for the propagation of the combustion. Reverberatory furnaces are naturally well suited for roasting, and many devices have been employed to increase their efficiency for this purpose. The long-bedded reverberatory has proved of great value. It may be 60 to 80 ft. long and 16 ft. wide and contain four hearths, which rise successively by a small step of 2 ins. towards the flue. Each hearth holds one charge of ore, and each charge is moved in turn from the cool charging end on to the next hearth nearer the fire-bridge, and is eventually discharged through a hole in the hearth adjoining the fire-bridge. By this means a slow rise of temperature is ensured and premature clotting of the ore and consequently arrested oxidation is obviated.

To surmount the heavy labour required in working this furnace, others of the reverberatory type are used in which the ore is stirred by mechanical contrivances, the arrangement being such that either the hearth revolves and the rabbles are fixed, or the hearth is stationary and the plough-shaped rabbles are dragged through the ore, turning it over and exposing fresh surfaces to the air.

Another ingenious method of bringing fresh ore constantly into contact with air is by the use of revolving cylinders, which may be 40 ft. long and 3 ft. in diameter. These turn very slowly around an axis, horizontal or sloping, according to the type used, and the charge inside slips directly its angle of repose is exceeded owing to the movement of the cylinder. Hot furnace gases and excess of air are drawn continuously through the cylinder.

Of recent years, entirely new methods of roasting lead ores have been developed, which differ from those just sketched in much the same way that blast furnace methods of smelting differ from reverberatory methods. These methods have become of great importance, especially in America, which is favoured by having vast supplies of suitable ores. In some respects they recall those of heap-roasting, the ore being first kindled and the main bulk of it roasted without the application of external heat, the sulphides acting as fuel and evolving heat by their oxidation. There is, however, the important difference that the air, instead of slowly permeating the charge unaided, is forced through under pressure, thereby diminishing the time of action. The original process was carried out in iron vessels called pots or converters and a blast of air was blown through the ore; from which circumstances the name of blast or pot-roasting has been applied to the process and its variants.

In the original process of Huntington and Heberlein (often referred to as the H.H. process), the ore was first partly roasted in a reverberatory furnace with about 10 per cent. of limestone. Part of this ore was maintained hot, the remainder allowed to cool, and then moistened with water. To complete the roasting, a conical-shaped iron pot, fitted with a grate and blast-pipe near the bottom, was used. A fire of wood or coal was kindled on the grate, the hot ore laid on top, the blast started and the cold ore gradually fed in, the pressure of the blast being slowly increased. Oxidation of the sulphide ore takes place and gradually spreads throughout the mass, the charge becomes agglomerated, and when, after some hours, the pot is tipped, the contents fall out as a solid block of porous material which, after breaking up, is in good condition for smelting in the blast furnace. By this method the ore is desulphurised and the lead left in the form of oxide and such oxidised compounds as the silicate.

A still more efficient mode of roasting is that invented by Messrs. Dwight and Lloyd, often termed the D.L. process, the chief merit of which is that it is continuous in action. The crushed ore is mixed with limestone and suitable fluxes, moistened with water to prevent loss by the blast, and fed to a depth of 4 ins. into a continuous series of boxes, each about 2 by 3½ ft., which travel on an endless chain. The bottoms of these boxes consist of a cast-iron grate, upon which the ore mixture rests. At a certain position in their course, each box passes a gas or oil burner which impinges on the surface of the ore and ignites it, and it then comes over a chamber from which the air is exhausted. A stream of air is thus sucked downwards through the ore and the roasting process is set up and speedily finished. After it has passed the exhaust chamber, the box is jerked by falling to the return cable and the cake of roasted ore shot out. The empty boxes then return to the charging point and the process is repeated. The rate of travel is slow, being about 8 ins. a minute. The gases drawn off from the exhaust chamber are rich in oxides of sulphur and may be used for the manufacture of sulphuric acid.

Smelting of the Ores. The blast furnace method is at present by far the most important one for the smelting of lead ores. The preparation of the ores for this purpose by roasting is an important preliminary step, and the methods used to this end are many and varied, as we have just seen. In general, these roasted ores form the main constituent of the charge for smelting. To them are added naturally-oxidised ores, like the carbonate ; ores rich in silver, the roasting of which is avoided in order to minimise loss of the precious metal by volatilisation ; fluxes, if necessary, though in general these are added to the roasting charges ; some slags from a previous operation, the function of which is to facilitate the running of the furnace, and coke for fuel and purposes of reduction.

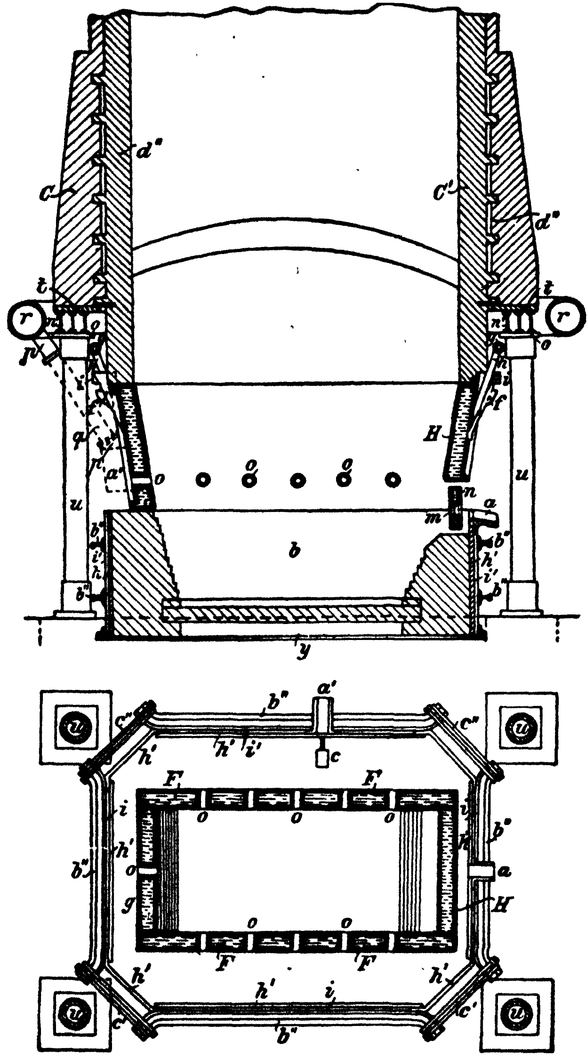
Great care must be exercised in selecting the right quantities of the various constituents of the charge, for, as already noted, the non-leady materials must unite to form a slag which is fusible; specifically light, so that it is easily separated from the other products of smelting; and free, or nearly so, from lead and silver. Slags are salt-like compounds formed by the union of basic and acidic oxides, and the slags produced in lead smelting are formed essentially from the two basic oxides, oxide of iron FeO, lime, CaO, and the acidic oxide silica, SiO_2. They are thus silicates of iron and calcium, and though considerable latitude in their composition is allowable, it is generally found expedient that they should contain about 64 per cent. of the oxides of iron and calcium, and 36 per cent. of silica. From the knowledge of the chemical composition of the materials to be used in smelting, the quantities of these can be calculated to fulfil the conditions requisite for the production of a suitable slag. It should be noted that the oxide of lead is itself basic and combines with silica, under favourable conditions, to form a slag of lead silicate; but the presence of carbon and iron prevents the slagging of the lead in this way, the former by reducing the oxide to metal, the latter by reacting with any silicate of lead which is present, liberating lead and forming silicate of iron.

The older forms of blast furnace were circular in cross section. As the effective limit of penetration of the blast is about 5 ft., these furnaces were restricted in size, since the diameter could not exceed this limit; in most cases it was less, averaging from 3½ to 5 ft. By building the furnaces with a rectangular cross-section, placing all, or most of, the tuyeres on the two longer sides, the capacity can be greatly exceeded, consistently with the maintenance of effective blast penetration. Such rectangular furnaces are largely used, especially outside of Europe, the dimensions at the tuyeres being commonly 3·5 ft. by 10 ft., or in extreme cases, 5 ft. 2 ins. by 17 ft. 8 ins.

Since lead is a volatile metal, it is necessary that the smelting furnace should not become too hot, and this condition is attained by the use of water-cooled jackets around the hottest zone and by lengthening the shaft, so that the furnace may work with a cool throat. Accordingly, these furnaces are constructed with a tall shaft, which has increased from 12 to 20 ft. in recent years. The tuyeres are usually placed at a height of 1 ft. above the level of the lead surface in the crucible, this provision being made in order to keep the metal as cool as possible, while still remaining molten. A sloping channel connects the lead in the crucible with a well outside the furnace. By this device, known as the syphon tap, the level of the lead in the crucible is kept constant, the metal ladled or run off from the well is cool and therefore not so susceptible to oxidation, and the disengagement of poisonous fumes is, in a large measure, prevented. The slags and mattes collect on the surface of the molten lead in the crucible, being specifically lighter, and are run off through the slag tap, which is placed a little above the level of the lead.

The charging is performed through doors near the top of the shaft and the furnace gases and fumes are drawn off through a wide pipe which leads to the dust chambers and thence to the stack.

The chemical reactions in the blast furnace are, in outline, as follows: Carbon of the fuel burns to carbon monoxide and carbon dioxide. The carbon monoxide and the heated carbon reduce lead oxide (PbO) to metallic lead and ferric oxide (Fe_2O_3) to ferrous oxide (FeO) and metallic iron (Fe). Ferrous oxide and lime unite with silica (SiO_2) and alumina (Al_2O_3) to form a slag of silicates and aluminates of iron and calcium. Lead silicate, produced either during the roasting or formed in the blast furnace from lead oxide and silica, reacts with ferrous oxide and iron with liberation of lead and formation of a slag of ferrous silicate. Lead sulphide (PbS) is partly reduced by iron, yielding ferrous sulphide (FeS) and lead; partly it enters into reaction with lead sulphate, as in the air-oxidation process, to produce lead and sulphur dioxide. If copper be present, it combines preferentially with sulphur and the sulphides of copper, iron and lead mix together readily and produce a "matte," which runs through the furnace, is tapped with the slags and, being heavier than these, is easily separated on settling. Such mattes can afterwards be treated as sulphide ores, being roasted and resmelted, or if rich in copper they can be worked for that metal. Arsenic, and to some extent antimony, if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Figs. 5 and 6

present, are volatilised. Most of the other heavy metals are reduced and pass into the lead, wholly or in part, and must be separated from it afterwards.

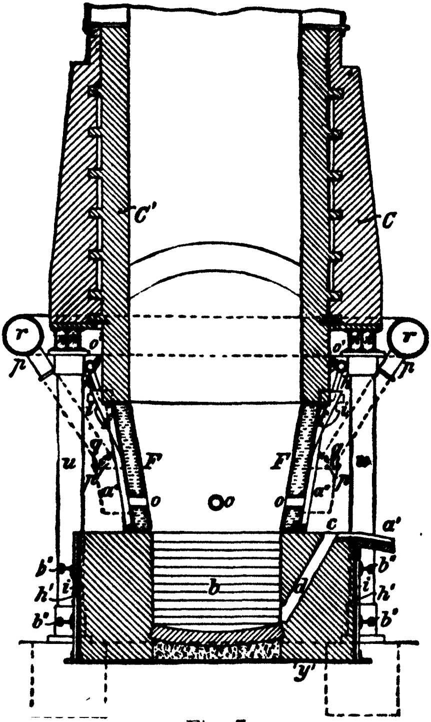


Fig. 7

Figs. 5, 6 and 7 illustrate some of the most important features of the rectangular blast furnace for smelting lead ores. Of these, 5 and 7 are sectional elevations, and 6 a sectional plan. The crucible in which the molten products collect is shown at *b* (Figs. 5 and 7), and the syphon through which the lead flows to a vessel outside the furnace at *d* (Fig. 7). The zone of fusion is cooled by wrought iron water-jackets F (Figs. 6 and 7), in which are holes O for the tuyeres. Slags flow away through a notch *m* provided with a water-jacket *n* (Fig. 5) ; *r* is the main blast-pipe from which the tuyeres are supplied. A portion of the shaft of the furnace, above the water-jackets, is shown in Figs. 5 and 7.

As an example of blast furnace smelting, the practice at Trail, British Columbia, may be cited. The sulphide ores, and mattes from previous smeltings, are mixed with limestone (calcium carbonate) and partially roasted in revolving hearths. The proportions of the chief constituents of the mixture are—

Lead (Pb) .	40–44	per cent.
Oxide of Iron (FeO)	10–13	,,
Silica (SiO_2) .	8–11	,,
Limestone ($CaCO_3$)	7–10	,,
Sulphur (S) .	14–17	,,

This is roasted until the sulphur is reduced to 8-9 per cent., then submitted to blast roasting to effect a further reduction of sulphur. The fully roasted and sintered ore is then smelted with coke and oxidised ores in blast furnaces of 45 ins. by 160 ins. cross-section at the tuyeres, the height of charge above the tuyeres being 17·5 ft., and the blast pressure 32 to 34 ozs. (equal to 56 ins. of water). The components of the blast furnace charge are—

Roasted Ore	85	per cent.
Coke	12·5	,,
Oxidised and Silicious Ores . .	2·5	,,

the charge averaging 40 per cent. of lead and 4 per cent. of sulphur.

The composition of the resulting slags is—

Silica (SiO_2)	31–33	per cent.
Lime (CaO)	18–20	,,
Oxide of Iron (FeO)	24–30	,,
Oxide of Zinc (ZnO)	7–12	,,
Alumina (Al_2O_3)	8–16	,,

and these slags carry 1 per cent. of lead and 0·4 ozs. silver per ton.

The crude lead (base bullion or work lead) contains 98·5 per cent lead; 0·22 per cent. copper; 0·098 per cent. zinc; 0·0133 per cent. bismuth; 0·28 per cent. arsenic; 0·32 per cent. of antimony, and 100 ozs. of silver, and 0·1 oz. of gold per ton. Each furnace yields 75 tons of lead per day.

The work lead obtained from different smelting houses naturally varies considerably in composition since this depends on the nature of the ores used and on the methods used in the extraction of the metal. The variations in composition are exhibited in the following table.

COMPOSITION OF WORK LEAD

Source.	Per Cent.						Ounces Per Ton.	
	Lead.	Antimony.	Arsenic.	Copper	Bismuth.	Sulphur	Silver.	Gold.
England	99·87	0·05	0·01	0·115	0·001	0·015	7	—
Spain	98·92	0·40	0·21	0·150	0·005	0·100	45	—
Germany	96·67	0·82	0·45	0·940	0·066	0·200	180	—
Greece	98·27	0·55	0·10	0·750	0·010	0·080	45	0·07
United States	98·50	0·32	0·28	0·220	0·013	—	100	0·10
Mexico	95·40	1·80	1·30	0·080	0·050	0·350	300	1·50

CHAPTER VIII

CONDENSATION OF LEAD FUME

IN the smelting of lead ore, loss is occasioned in two ways ; firstly, by the decrepitation of the ore on heating and the removal of the fine particles in the draught; secondly, by the escape of lead compounds which have been volatilised. It has already been pointed out that galena is volatile at a high temperature, and the same statement may be made in regard to lead itself, especially in contact with air, and some of the compounds of lead, notably the oxide. The result of this volatility is the steady disengagement of large volumes of smoke or fume, consisting chiefly of oxide and sulphate of lead suspended in air, from all furnaces in which lead and its ores are treated. Notwithstanding the high density of these compounds, they settle very slowly, owing to their exceedingly fine state of division, and unless they are condensed the loss of lead becomes a serious matter to the smelter. Other volatile metals present in the ores, particularly arsenic and zinc, are also present in the fume, and on occasion they form a considerable part of it.

Equally serious is the effect of this fume when it escapes into the air, for in time it settles out on the land, the oxides of sulphur which accompany it are dissolved and washed down in rain and the combined action of these is highly inimical both to animal and vegetable life. Altogether, the conjunction of smelting and lead-mining, with its accompanying unsightly heaps of barren spoil material and the pollution of the streams by mud from the washing plants, has a very detrimental effect on the country, and one is not surprised to read that "there were periods when the limestone district (the lead raising and smelting area) of Derbyshire was a vast mining waste." Large sums are often paid in compensation for damage done in this way, and frequent litigation becomes irksome. To avoid "smoke-suits" (as they are called in America) the land in the neighbourhood of the smelting works is often bought up.

It is, of course, more rational to take steps to avoid or, at any rate, to minimise the trouble than to accept it calmly as a necessary evil, and it not infrequently happens in such cases that the advantage gained by retention of the obnoxious material far outweighs the labour and expense undertaken in the investigation of the problem and the erection of suitable condensing plant. Legislation, once necessary to prevent the escape of hydrochloric acid from salt-cake works, is to-day almost or quite superfluous, since the manufacturer has found that it pays to recover his hydrochloric acid. It is very probable that, in the near future, the black pall of sooty smoke, which hangs over many towns, will be banished, and it is safe to forecast that this will prove of benefit, not only to the blameless inhabitants, but also to those who, in their wastefulness and indifference to the well-being of others, are the cause of the nuisance.

The condensation of lead fume is part of the much larger problem of removing solid matter in a state of fine sub-division from air. Given sufficient time, the fume will eventually settle, but the main difficulty is to cope with large volumes of air in which the solid is dispersed in such a way that storage-space of excessive size is obviated.

One of the pioneers in the condensation of lead fume was Dr. Watson, Bishop of Llandaff, a chemist distinguished particularly by his writings on the history of the science and by his investigations on lead ores and lead smelting. He suggested in 1778 that the lead fume "might be collected either by making it meet with water, or with the vapour of water, during its ascent, or by making it pass through a horizontal chimney of suitable length." Such a chimney built for another purpose at Middleton Dale, in Derbyshire, was adopted for a trial on Watson's advice and proved its utility. The use of these long flues has been extensively developed, the total length of some attaining to many miles. They are usually 8 ft. high and 6 ft. wide, and frequently follow zig-zag courses along a hill side, the chimney which supplies the draught standing on the top of the hill. They are cleaned out at fairly long intervals and the openings then bricked up.

With a view to exposing a larger surface for the precipitation of the fume and to the breaking up of the direct currents of gas, various devices have been tried, such as the building of baffle walls, the hanging of metal plates and the interposition of screens of wire in the flues and dust chambers. None of these measures has been attended with great success, and the resistance to the passage of the gases by their use becomes so considerable that the ordinary chimney draught has to be supplemented by exhaust ventilation.

Watson's suggestion of the use of water or steam for the precipitation of fume has been tried in a very thorough manner, but without complete success. Though at first sight the methods seem promising, especially the injection of steam into the fume, and its subsequent condensation, yet experience has shown that it is a difficult matter to wet a fine dry powder, and a mist of water or other liquids is not easily condensed. Among the methods tried may be mentioned: bubbling the fume through tanks of water; passage through wet filters made of faggots or cobble-stones resting on grids, and the use of artificial rain or sprays of water, sometimes combined with filtering devices. Long experience with these methods, all of which have been attended with a limited measure of success, has emphasised the important fact that condensation of fume is best achieved in the dry state, and it is to methods in which this fact is recognised that we shall now turn our attention. Of these the two most important are dry filtration and electrical precipitation.

The idea of filtering dry fume through textile fabrics was suggested by John Percy, the eminent metallurgist, in 1870, and was developed in comparatively recent years into a technical method, chiefly by American smelters. The filters consist of bags, 25 ft. long, and 18 ins. in diameter, made of cotton or wool. These are hung in great numbers in a spacious bag-house, the lower, open ends being fitted round orifices in the floor. Under the floor is a chamber connected with flues. The gases and fumes from the furnaces pass, sufficiently cooled from the flues, into this chamber, and thence through the bags, and the filtered gases escape by ventilators in the top of the bag-house. In passing through the bags the solid fume is retained by the fabric and can be detached periodically by shaking the bags, or by causing them to collapse by temporarily exhausting them. The dust falls to the floor of the lower chamber where, being feebly combustible, it is usually kindled and allowed to burn in a current of air. It can then be removed in an agglomerated or clinkered form, suitable for working off with the ordinary smelting charges.

The capacity of these bag-houses is often great. In Utah, for example, no less than 165,000 cubic feet of fume-bearing gases are filtered every minute, the total filtering surface being 570,000 square feet. A house may contain hundreds, or even thousands, of bags. The fabrics present some difficulty, since they are attacked by acid fumes, and the method is most successful where these are present in small quantities. In general, it is not applicable to gases from the roasting furnaces, which are rich in oxides of sulphur. Woollen bags, especially unwashed ones, are most durable, lasting up to four years; cotton bags only endure about one-third of that time. By the adoption of bag filtration, 1 per cent. or more of the lead in the charge, which would otherwise be lost, may be recovered. A typical bag-house fume contains 50 per cent. of lead, 14 per cent. of arsenic, 3 per cent. of zinc, and 5 per cent. of sulphur, and the metals are present chiefly as oxides, partly as sulphides and sulphates.

The electrical precipitation of fume is a method of recent development. That an electric discharge clears a smoky atmosphere is a fact which has been known almost for a century. It appears to have been forgotten, however, until 1883 when Sir Oliver Lodge carried out many experiments on the subject and made suggestions as to its possible use in practical life. In Lodge's words, " The rapidity with which an electrified point clears the box of smoke is so noticeable as to suggest several practical ideas. . . . The electrical cleaning of the air of smoke-rooms, or of tunnels, is, perhaps, not an impracticable notion."

The application of the method to the treatment of lead fume was not long delayed, for two years later the method was tested by Hutchings at Deebank, in Wales, though without much success owing, as was subsequently apparent, to the small power employed. In the later development of the subject, much credit is due to Cottrell in America and Lodge in England.

The first commercially successful process was worked out only about ten years ago.

When a high-tension electric discharge takes place from a point, particles in the neighbourhood become electrically charged and are attracted to surfaces of opposite polarity. Solid particles of lead fume suspended in air would thus, in these circumstances, be repelled from the charged point and precipitated on an electrode of opposite electrical sign. This is, briefly the principle of the process ; the technical difficultie are the production of very high, direct current voltages and the construction of a plant capable of dealing quickly with vast volumes of fume-laden gases. To produce a suitable glow-discharge, low voltage alternating curren is transformed into high voltage alternating, and thi is then " rectified " or converted into intermittent high voltage direct current. The methods by which this i achieved do not concern us here.

The precipitation plant, in one practical form, consist of a number of iron pipes, 20 ft. long and 1 ft. i diameter, which serve as collecting electrodes and ar earthed ; axially within these pipes hang the carefull insulated discharge electrodes, negatively electrified a a tension of some 100,000 volts. The gases cours through the pipes, the fume is precipitated on th inside surfaces and is readily detached by striking th pipes periodically with a hammer. An installation a Trail, British Columbia, capable of dealing with 100,00 cubic feet of fume a minute has 384 pipes.

The method, with suitable modifications, is a genera one, and can be applied to all cases of industrial smok and fume, where the particles are solid and dry, as we as to mists, such as those produced in the manufactur of oleum, and to liquid emulsions.

CHAPTER IX

SOFTENING AND DESILVERISATION OF WORK LEAD.

THE lead produced in smelting, particularly by the blast furnace, is generally impure ; it is known as work lead or base bullion and contains various quantities of the metals associated with the lead ores. Chief among these impurities are the metals zinc, copper, iron, tin, arsenic, antimony, bismuth, and silver; of these the first three are only soluble to a limited extent in lead, while the remainder mix with lead in all proportions. The general effect of these metals is to render the lead hard and unsuitable for many purposes to which lead is applied. The removal of the impurities thus brings about a softening of the lead and is a necessary process for the production of the commercial metal, and also as a preliminary in the extraction of the precious metals, silver and gold.

The occurrence of silver and gold in lead ores has already been mentioned, and it is a fact of the utmost importance that in smelting lead ores the precious metals pass into the work lead and are recoverable from it. In fact, one of the objects of lead smelting is to collect the silver present in argentiferous lead ores and in silver ores proper, which are added to the furnace charges, the lead being used as the solvent or vehicle for the extraction of the precious metals. The amount of silver present in lead ores varies greatly; from 0·1 to 1·0 per cent. may be regarded as common limits, but some ores, like those of Missouri and Carinthia are practically non-argentiferous, while at the other end of the scale, it is difficult or impossible to state when a particular ore ceases to be a lead ore and becomes a silver ore. From these circumstances arises the custom of referring to certain mines and furnaces as silver-lead mines and silver-lead furnaces.

To avoid the use of small fractions, it is customary to state the composition of ores and furnaces products not in percentage amounts of silver, but in terms of ounces Troy of silver per ton of material. As 1 short ton (2,000 lbs.) contains 29,166 ozs. Troy, 0·1 per cent. of silver is equal to 29 ozs. per ton. The sub-divisions of the oz. Troy are the pennyweight (dwt.) of which there are 20 to the oz., and the grain (gr.) of which there are 24 in the pennyweight. The amount of gold in lead ores and furnace products is very small, though often capable of profitable extraction. It behaves almost exactly like silver in the various extraction processes and is finally obtained as an alloy of silver and gold. In the account of these processes which follows we shall concentrate attention upon the silver.

In the softening (also known as improving) of hard lead, one or more processes may be adopted according to the nature of the metal. If the molten lead be allowed to cool slowly, the impurities only partly soluble in it settle out to an extent depending on their degree of solubility, and can be removed. Again, if the crude lead be cast in pigs and these heated in a smoky flame on the sloping floor of a reverberatory furnace, the more easily fusible lead sweats or melts out of the pigs and is collected in the well of the furnace, whilst the higher melting metals and alloys remain behind. This process is known as liquation.

Finally, when a mass of molten, impure lead is freely exposed to the air, oxidation both of lead and impurities takes place. The oxides formed, being insoluble in the lead and lighter than it, arise to the surface as a scum or dross and are skimmed off. By the continuance of this oxidation process for a sufficiently long time, most of the impurities are removed, along, of course, with a certain amount of lead oxide, and the remaining lead is soft enough for most commercial purposes and for desilverising.

The drosses from the improving furnace and the liquation residues are rich in lead and the original impurities, and must be further treated in order to extract these metals, either singly, or in the form of such desirable alloys as antimonial lead.

Of recent years, a radically different method of refining work lead has been developed and successfully put into operation. The method is an electrolytic one, a suitable current being passed through the solution of a lead salt, the anode consisting of slabs of work lead, the cathode of thin sheets of pure lead. Under these conditions, lead is dissolved from the anodes and precipitated pure upon the cathodes, but the impurities in the anode lead do not pass into solution. They form a mud, known as the anode slimes, which is collected and treated for the extraction of precious metals.

It is of the greatest importance that the electrolyte should be a salt of lead, easily soluble in water, the solution having a high conductivity for the electric current, and that such compounds as lead peroxide should not be formed during electrolysis. These conditions are satisfied by lead fluosilicate but not by the more commonly known salts, such as the sulphate, nitrate, chloride, and acetate, and it is by the use of this fluosilicate that the electrolytic process has become practicable. It may be added that the salt is easily made from hydrofluoric acid (prepared from fluospar and sulphuric acid), silica, in the form of quartz, and white lead.

The mutual relations of silver and lead have been referred to several times, and it may be well to summarise them here before passing to the description of the methods used in desilverising argentiferous lead. Almost all lead ores contain silver, either native, that is as metal, or in the form of some compound, such as the sulphide or chloride. When lead ores are smelted, metallic silver, whether originally present or liberated from its compounds in the smelting process, passes into the molten lead, being easily and completely soluble in that metal. The work lead produced by smelting contains, therefore, practically all the silver originally present in the charge, and this silver remains in the lead during the many processes which the work lead may have to undergo in order to fit it for the market. The reasons for this are that silver does not form high-melting alloys with lead and the other metallic impurities and is therefore melted out with the lead during liquation; further, it is not oxidised when heated in air, and thus does not rise with other metallic oxides as a dross in the softening furnaces.

All processes of purification of the crude lead, therefore, leave the silver with the purified metal and the problem of separating the silver then arises. One method of effecting this separation has already been considered, namely, the electrolytic method, in which the silver, mixed with the other foreign constituents, is concentrated in the anode slimes ; from these it can be recovered without much difficulty. This method has been in use for little over twenty years. The extraction of silver from silver-bearing lead has, however, been practised for more than twenty centuries, and until a little less than a century ago was based entirely upon the difference in chemical behaviour of lead and silver towards the oxygen of the air. Silver, when melted in air, remains undimmed in lustre and unaltered in properties; lead, on the other hand, becomes coated with a pellicle of litharge or lead monoxide, Pb O, formed by chemical union of the metal with oxygen. This oxide can be removed from the surface, or absorbed by the hearth on which the molten metal rests and in time all the lead becomes converted into litharge. When an alloy of the two metals is oxidised in this way, the lead is gradually drossed, the silver remaining in solution with the unaltered lead, so that the alloy becomes steadily richer in silver, and eventually all the lead is oxidised and the pure silver remains.

This is the basis of the cupellation process—a process of the greatest antiquity, mentioned in the earliest written records, and without doubt the final stage in the operations whereby the ancients obtained the greater part of their silver from lead-silver ores. As the litharge formed in this process can be made to yield up its lead easily by reduction with carbon, the separation of lead and silver from their alloys is readily effected.

The labour and cost of cupellation are naturally considerable, and it used to be held that the lead should contain at the least 8 ozs. of silver per ton to make the recovery of the silver profitable. In this regard much depended on the skill of the operator, and at one period the fame of the refiners of the Netherlands was in such repute that much English lead was sent there for cupellation. Thus we read of a royal grant to certain "burges of Edinburgh" in 1562, "to work and wyn in the leid mynes of Glengonar and Wenlock and to transport and carie forth of this realm to Flanderis. . . twenty thousand stane wicht of the said leid ure," the condition being the delivery to the Queen's Majestie of "fortie-five unce of uter fyne silver for every thousand stane wicht of the said leid ure."

It is clear that any method whereby the silver could be concentrated in a portion of the lead, leaving the remainder of the lead free from silver, would be an advantage, since not only would the oxidation of much lead in the cupellation furnace and subsequent reduction of an equivalent amount of litharge be avoided, but also it would be possible to extract the silver from lead too poor in the precious metal for direct cupellation; this silver would naturally otherwise be lost.

Two methods of effecting this desired end were invented in the last century. In that of Pattinson (1833) the silver-lead alloy is concentrated by crystallisation and the rich alloy cupelled. In the process of Parkes (1850) the silver-lead alloy is mixed with zinc and a triple alloy of zinc, lead and silver obtained, all of the silver passing into this alloy. The triple alloy is then distilled to remove the volatile zinc and the residual lead-silver cupelled. In both cases, therefore, though the processes are radically different in principle, a rich alloy of silver and lead is produced and only this is cupelled, the bulk of the lead escaping this operation.

The Pattinson Process. Mention has already been made of the solubility of silver in lead, and the term is no misnomer for the liquid alloy of the two metals behaves in many ways like a solution, say, of common salt in water, lead and water being regarded as the solvent, silver and salt as the solute or dissolved substance in the respective cases. Everyone knows that the freezing point of water is lowered by the addition of salt, for brine freezes at a lower temperature than pure water, and salt is used for melting snow and ice. Similarly, the melting temperature of lead (327° C.) is reduced by the addition of silver, the minimum melting point obtainable being 303° C., and the alloy then contains 2·5 per cent. of silver. This alloy, having the lowest melting point of any mixture of lead and silver, is called the eutectic (*lit.* best melting) alloy.

Now when brine is frozen, pure ice separates and consequently the residual liquid becomes richer in salt. If the freezing be continued, the temperature being progressively lowered as the concentration of the liquor increases, a eutectic mixture of salt and water is at length produced; on further reduction of temperature this mixture freezes as a whole at constant temperature and no further separation of ice and salt is possible. The cooling of a molten lead-silver alloy shows a perfectly analogous behaviour. Pure crystals of lead first separate, the residual liquor becoming richer in silver, and a reduction of temperature becomes necessary to freeze this richer alloy. When the silver content rises to 2·5 per cent. separation of the two metals becomes impossible by crystallisation and the eutectic alloy freezes as a whole.

This is the basis of the Pattinson process. Molten work lead is allowed to cool slowly, the crystals of pure lead are fished out and the rich residual alloy is eventually cupelled. The limits of concentration of the silver are naturally fixed by the composition of the eutectic mixture, that is, the alloy cannot be enriched by this process so that it contains more than 2·5 per cent. of silver. In actual practice, the enrichment is a good deal less than this figure and further, since it is impossible, even by careful draining, to remove completely the argentiferous alloy from the lead crystals, the crystallising process must be repeated several times in order that the desired end may be attained.

The practical method of working the process is as follows. The work lead is melted and crystallised in hemispherical, cast-iron pots, each holding about 10 tons of lead and fired separately. These pots are arranged in a row or battery, from 8 to 15 in number. and the work is so carried out that the desilverised lead travels in one direction and eventually comes to the end or market pot, the enriched alloy passing in the opposite direction. A charge of work lead is melted down in one pot and skimmed. The fire is withdrawn and the metal allowed to cool; any crusts which may form at the sides of the pot are barred down, the metal is thoroughly stirred and cooling is hastened by spraying water on the surface of the lead. When crystals of lead are formed, they sink and are fished out by a perforated ladle (see Fig. 9), allowed to drain a few minutes and transferred to the pot on the right. After two-thirds of the metal have been withdrawn in this manner, the enriched residue is ladled to the pot on the left, a fresh charge placed in the original pot, and the process repeated,

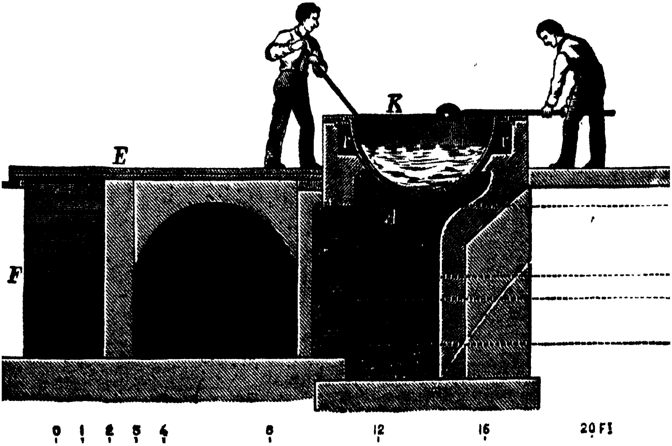


Fig. 8
THE PATTINSON PROCESS

K (Fig. 8) represents a pot holding 12·5 tons of silver-lead. The flames from the fire at A strike the bottom of the pot and are drawn through a flue *v* which surrounds the upper part of the pot. The actual operations of fishing out the lead crystals and allowing them to drain in the perforated ladle are shown in Fig. 9.

The other pots in the series are treated in a similar way when they become full, either by the fractionation of a work lead of uniform composition, or by the addition of work lead containing an amount of silver appropriate to a particular pot in the series. A practical example will illustrate the progress of enrichment and impoverishment of the argentiferous lead. Work lead assaying 21 ozs. of silver per ton is pattinsonised in a battery of 10 pots, of which No. 1 is the market pot, No. 6 the charging pot, and No. 10 the rich lead pot. The assay of the contents of these pots is given in the diagram below—

Pot . . .	10	9	8	7	6	5	4	3	2	1
	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	ozs.	dwt.	dwt.
Silver per ton of lead	220	129	79	41	21	11	4	2	18	9

Two-thirds of the contents of pot 6 are allowed to crystallise and removed to pot 5, the remaining third of enriched lead is ladled to 7. A fresh charge is brought into 6 and fractionated in like manner. When 5 is full it is treated in the same way, two-thirds passing to 4, and one-third back to 6, and so on through the series, the silver content of each pot being kept approximately constant. Thus No. 1 becomes the receptacle for desilverised lead, fit for the market, and No. 10 for the rich alloy which can be profitably cupelled in order to recover the silver.

In this process, often called hand-pattinsonisation, it will be noted that the crystals of lead are lifted from the bottom of the pot where they gather together, and transferred by hand labour to the adjacent pot, and the stirring also, which is essential to promote good crystallisation, is done by hand. In the modification due to Luce and Rozan, the stirring is accomplished by blowing dry steam through the molten alloy. The crystals are allowed to subside and the still molten, enriched lead-silver alloy is run off, leaving the desilverised lead behind. This process reduces the labour of pattinsonising; like the original process it must be carried out in a systematic manner. Another, more recent modification is to support the large crystallising pots on hydraulic rams, so that the liquid alloy, and

Fig. 9

DESILVERISATION OF LEAD BY THE PATTINSON PROCESS the residual lead, after remelting, can be run into the appropriate neighbouring pots by simply tilting the containing vessel.

The Process of Parkes. This is a desilverising process in the simplest sense, for the silver is withdrawn from base bullion by the direct action of the metal zinc. The relations of solubility subsisting among the three metals chiefly concerned in the process are important and deserving of attention, in order that the process may be understood. Silver dissolves in all proportions in lead and zinc, but preferentially in the latter metal, possibly owing to the formation of definite compounds of the two metals. Lead and zinc, on the other hand, are only soluble in each other to a limited extent, the solubility at 350° C. (*i.e.*, a little above the melting point of lead) of zinc in lead being 0·6 per cent. and of lead in zinc 1·7 per cent. When the two molten metals are mixed in sufficient quantities and then allowed to remain some time at rest, separation into two layers takes place, the lower being lead saturated with zinc, the upper, zinc saturated with lead.

Now when zinc is mixed with molten silver-lead alloy (base bullion), and the metal allowed to stand, separation takes place and the lower layer consists of lead saturated with zinc, the upper of zinc saturated with lead and containing, in addition, the silver, which dissolves by preference in the zinc. As the upper layer has a higher melting point than the lower, it solidifies first on cooling, and the crust of the triple alloy of zinc, silver and lead can be removed and treated for the extraction of silver. The residual lead is free from silver but contains about 0·6 per cent. of zinc ; after removal of the zinc it is fit for commercial use.

The operation of zincing, or extraction of the bullion lead with zinc, is performed in cast-iron pots, holding up to 60 tons. These are circular and may be 10 ft. in diameter, and 3 ft. 6 ins. deep, each pot being separately fired. The lead is run from the softening furnace into the pot, skimmed and heated somewhat above the melting point of zinc (418° C.). Zinc is added, either solid or molten, in quantity determined by the amount of silver in the work lead, well stirred in either by hand or by a mechanical stirrer, and the bath allowed to cool. The crusts of triple alloy are taken off with a perforated skimmer and drained. Sometimes they are freed from adhering lead by squeezing in a mechanically-worked press (Howard's press).

The weight of zinc necessary for the extraction of the silver varies from about 1 to 2 per cent. of the weight of lead, and may be added all at once or, as it is more usual, in two or even three batches. When two zincings are done, the first crust contains the bulk of the silver, and the second, being poor in silver, is added to a fresh pot of base bullion, along with enough zinc to make up the requisite charge.

The composition of the zinc crusts varies considerably, but may be roughly reckoned as 80 per cent. of lead and 20 per cent. of zinc and silver, zinc predominating over silver.

Of the three metals which compose the zincage crusts, only zinc is easily volatile, the pure metal distilling at 670° C. Accordingly the zinc is removed by distillation, the crusts being packed into a stout graphite retort, connected by a luted hood to a sheet-iron condenser placed outside the furnace and the retort strongly fired. About 50 per cent. of the zinc is condensed in this way, and is used again in the process. The residue in the retort is ladled out, after removal of the hood and condenser, and cast into bars. These distillery bars, as they are termed, may contain from 2,000 to 5,000 ozs.

of silver per ton, and the silver is recovered from them by cupellation.

The desilverised lead in the zincing pots, after removal of the crusts, is run into the softening furnaces, the dissolved zinc removed by oxidation with air or steam, and the resulting metal is then marketable.

The older Pattinson process for the extraction of silver from work lead has been in large measure supplanted by Parkes's process, as the latter has proved to be more economical ; the extraction of silver is more efficient, the market lead is purer and contains less silver (4 to 6 dwts. per ton by the Parkes', as against 9 to 15 dwts. by the Pattinson method) and the lead bullion for cupellation is richer (2,000 to 5,000 ozs. of silver per ton as against 500 to 650 ozs.). Another advantage which Parkes's process possesses is that traces of gold can be removed from lead by treatment at first with a small quantity of zinc (0·07 per cent.), insufficient to saturate the lead. After removal of the gold-bearing crust, the ordinary zincings for silver can then be carried out.

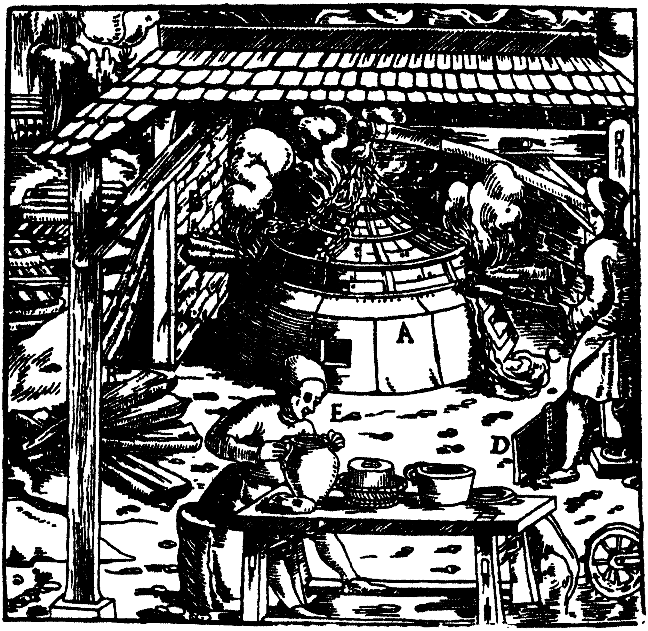
CHAPTER X

CUPELLATION OF ALLOYS OF SILVER AND LEAD

CUPELLATION, the final stage in the extraction of silver from argentiferous lead, is the process in which the molten alloy, resting on a suitable hearth, is exposed to a blast of air ; the lead is converted into litharge (Pb O) which is run off or absorbed by the hearth, and the silver, unaffected in these conditions remains on the hearth. The word is derived from the Latin *cupellum*, a little cup, and a cupel is the small cup-shaped vessel in which the operation of separating silver from lead is performed for the purposes of assay. The larger cupels or cupellation hearths used for metallurgical purposes are called " tests."

It has already been mentioned that cupellation is a process of great antiquity and Biblical references to it are common. There is direct evidence that it was extensively employed by the ancient Greeks at the famous mines of Laurium, which in one year (484 B.C.) yielded no less than 83,700 ozs. Troy of silver. It is described, though evidently without full comprehension, by Pliny and others of the ancient authors, and in considerable detail by Agricola and other representatives of more modern metallurgy.

The material of the hearth used in cupellation is an important matter since litharge when molten and at a high temperature is very reactive, chemically speaking, and readily corrodes fire-brick and such refractory materials. Bone-ash has proved a valuable material for the construction of the tests and cupels, for it is not corroded by litharge, and though it absorbs the molten oxide readily, it is impervious to silver. Lixiviated wood and plant ashes, and certain marls or calcareous muds, and the somewhat similar Portland cement are also used for the same purpose. There was a prejudice against the use of the ash of pigs' bones as material for making cupels and tests, though upon what grounds it is difficult to say. The old recipes often make specific mention of the ash from beef and mutton bones,



Taken from Agricola's "De re metallica" (1556)

Fig. 10

CUPELLATION

A represents the furnace with a movable roof, B sticks of wood for firing. The foreman, E, is engaged in eating butter as a specific against lead poisoning.

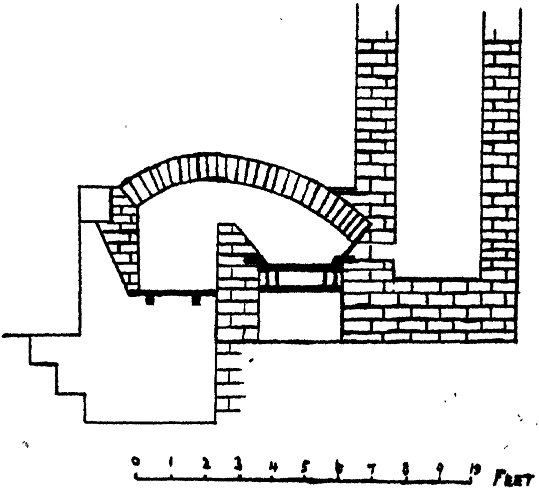


Fig. 11.

CUPELLATION FURNACE (ENGLISH)

This section shows the large fireplace on the left, the chimney on the right, and the small hearth between.

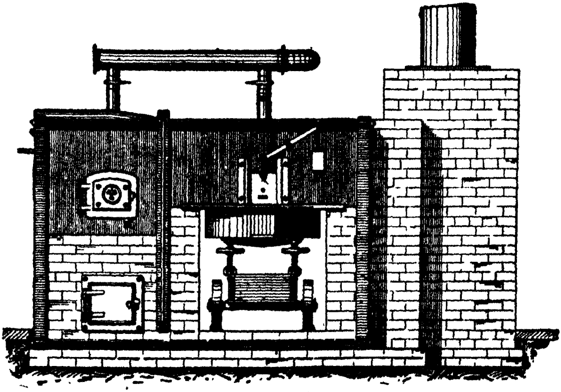


Fig. 12.

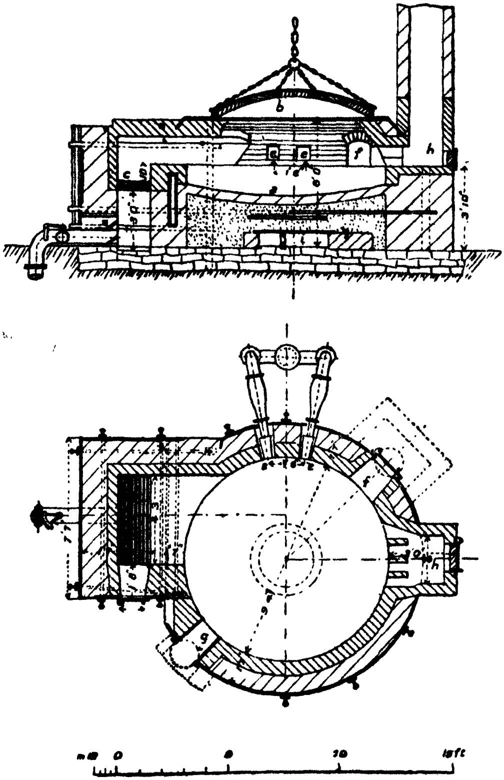
CUPELLATION FURNACE (ENGLISH)

Front elevation showing, in the middle, the carriage upon which the hearth

The furnace employed is a reverberatory, the heating of the charge being, therefore, from above. The fire-grate is large compared to the size of the hearth (*v.* Fig. 11), since a high temperature has to be maintained for a long time. The air necessary for oxidation of the lead is supplied through a tuyere, so placed that the blast impinges on the surface of the metal. This blast fulfils the added function of blowing the molten litharge towards the "brest" of the test, whence it runs off through a channel and is collected in a receptacle outside of the furnace. As a certain amount of litharge is absorbed by the hearths, they are broken up on renewal and sifted; the fine unaltered portions are used again, and the parts soaked with litharge are smelted in order that the lead may be recovered.

To facilitate the renewal of the hearths or tests, one of two alternative devices is adopted. In the English method of cupellation, the test is movable and can be placed in position or withdrawn with ease, being supported on a wheeled carriage (*v.* Fig. 12). In the German method the test is fixed, but the roof of the furnace can be raised and moved aside, thus giving access to the hearth.

The test for the English furnace consists of an oval frame of wrought iron called the test-ring, with a skeleton bottom of flat bars. Sifted bone ash is moistened slightly, well beaten into the ring and smoothed off. A shallow, saucer-like depression for the reception of the alloy, is then cut in this, along with a narrow channel (or gateway) across the front or brest of the test; this channel serves as an exit for the molten litharge. The test is thoroughly dried, heated strongly in position and filled with molten lead. When the blast is turned on, litharge is blown towards the brest and escapes through the gateway. As the lead is removed by oxidation, its place is supplied by the melting down of pigs of metal introduced at the back of the furnace.



Figs. 13 and 14
CUPELLATION FURNACE (GERMAN)

Fig. 13 is a sectional elevation. Fig. 14 a sectional plan of the furnace. The movable roof, hung on chains, is shown at *b* (Fig. 13), the fire-grate at *c*, the flue at *h*, the working-doors at *f* and *g*; the circular hearth lies between grate and flue. The tuyeres *e e* for the oxidation of the lead direct the blast across the course of the hot gases from the fire grate. The molten litharge flows away continuously at *g* (Fig. 14).

It is customary to work cupellation in two stages, in the first of which an alloy concentrated to 60–70 per cent. of silver is produced. This is then cupelled by itself on a separate test until all the lead is removed and a mass of pure silver remains. The litharge produced in the second stage contains a little silver and is gathered separately from the main bulk of litharge, which is but slightly argentiferous. The temperature of the finishing stage must be higher in order that the rich alloy, the melting point of which approaches that of pure silver, 961° C., may not freeze; should this happen, it might be very difficult to melt the alloy again.

If the silver contains metallic impurities, it is refined by exposing for a long time to the blast, the metal being maintained in a molten condition. The impurities are thus oxidised and rise to the surface of the silver. Sometimes an oxidising agent like Chili saltpetre ($Na\ NO_3$) is added in order to facilitate oxidation of the base metals. Molten silver absorbs oxygen and on solidification of the metal, this oxygen breaks away through the crust, forming crater-like excrescences and sometimes shooting forth particles of silver to a considerable distance. This phenomenon is known as the "spitting" or "sprouting" of silver. To hinder it, charcoal is sometimes placed on the surface of the metal before it solidifies.

When the work lead contains an appreciable amount of gold, this may be concentrated in the Parkes's process by preliminary treatment with a limited quantity of zinc. The gold crusts are then worked separately and eventually yield on cupellation a " doré bullion " which may contain 3 per cent. or more of gold. This is submitted to a parting process, whereby the gold is separated from the silver.

Before concluding this brief account of cupellation, particular mention should be made of the important property which litharge possesses of fluxing other metallic oxides, not of themselves fusible. For example, one part by weight of oxide of copper is liquefied by 1·8 parts of litharge; one of infusible zinc oxide by 8 of litharge, and so forth. Thus, if limited quantities of such base metals as zinc and copper are present in silver-lead alloy, they are oxidised along with the lead, and in part by the lead oxide which is an oxidising agent, and removed in solution with the molten litharge.

Thus it comes about that impure silver or gold can be refined by heating them with lead on the cupellation hearth. This method of refining precious metals has been used from the earliest times. Related to this, is the practice of extracting silver from true silver ores by feeding them into the bath of molten lead during cupellation. The silver of these ores dissolves in the lead, the base metals become oxidised and fluxed, and the silicious and earthy constituents are either fluxed by the litharge and carried away, or separate out on the surface of the bath and are raked off.

We can now summarise the relations of silver and lead in a few words. Nearly all lead ores contain silver which, in the process of smelting, passes into the liberated lead. True silver ores are also sometimes added to lead-smelting charges, as a convenient means of extracting the precious metal. The work lead or base bullion derived by smelting lead ores contains, in addition of silver, numerous metallic impurities. In general it has to be softened by oxidation, the impurities being removed as a dross or scum of oxides. Very rich work lead may be cupelled directly in order to recover the silver ; usually, however, the silver is first concentrated, and this may be effected by submitting the softened lead, either to Pattinson's or Parkes's process, the final result of each being that practically all the silver of the work lead is concentrated in a rich lead-silver alloy, which is then cupelled. In the electrolytic refining process, the crude work lead is directly treated, pure lead extracted, as it were electrically, and a residue obtained which contains all the impurities. This residue is then worked for the extraction of silver.

CHAPTER XI

PROPERTIES AND USES OF LEAD AND ITS ALLOYS

COMMERCIAL lead is generally of a high degree of purity; this is the result partly of the processes to which it is submitted specifically for this object, and partly of the further refining which takes place during desilverisation. Even small quantities of admixed metals, such as antimony, arsenic, copper and zinc harden it and render it unsuitable for many purposes, as well as interfering with the desilverising of the metal. In the following table are given analyses of some commercial leads which exemplify their high grade of purity. In may be remarked that the lead in the analyses is determined by difference, not directly estimated.

ANALYSES OF COMMERCIAL LEADS.

	English.	Australian (Ordinary).	Australian (Special).	Electrolytic Lead.
Lead . .	99·9919	99·9917	99·9977	99·9861
Copper .	0·0003	0·0001	0·0003	0·0027
Arsenic .	—	—	—	0·0025
Antimony .	0·0040	0·0060	0·0005	—
Bismuth .	0·0005	—	0·0006	0·0037
Zinc . .	0·0015	0·0010	0·0007	0·0018
Iron . .	0·0015	—	—	0·0022
Silver . .	0·0003	0·0012	0·0002	0·0010

The outstanding properties of lead are its softness, high density, low melting point and comparative unalterability in air at ordinary temperatures. Many of these properties are suitably modified by alloying with other metals, and accordingly we find that the uses of lead and its alloys are very extensive. Some indication of these will be given in the following pages. The metal is so soft that it marks paper, and can be indented with the finger-nail. If a seal of ordinary sealing wax be placed between two sheets of lead and a sharp blow be struck, the lead takes the impression of the seal.

Lead is very malleable and can be beaten or rolled out into sheets and, when hot, can be forced or squirted through a hole. These properties are illustrated in the making of sheet-lead and lead piping.

Sheet-lead used to be cast, the molten metal being poured from a gutter down a sloping table covered with sand, slightly damped and smoothed down, the excess of lead being caught by a gutter at the lower end of the table. For small articles, such as the straps used in white lead manufacture, the method of casting is used at the present day, a ladleful of metal being poured on to a slab, protuberances above the level of the slab supplying what perforations may be necessary in the straps. With experience, such thin sheets can be made with great ease and uniformity of thickness. The preparation of sheet-lead by rolling or milling came into use in England in 1670, and the method was vigorously opposed at the time. The operation is a simple one, an ingot of lead being passed backwards and forwards through the rolls until of the required thickness.[1]

Sheet-lead is extensively used for roofing purposes and lining tanks and gutters, and at one period was employed as a sheathing for ships, for which purpose, however, it does not appear to have been a great success.

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[1] The thickness of milled sheet lead varies from one-twentieth to one-fifth of an inch, and the size of the sheets from 20 to 40 ft. long by 6 ft. 9 ins. to 9 ft. wide. Sheet lead is classified according to the weight per square foot; when 1 sq. ft. weighs 5 lbs., for example, the lead is known as 5 lbs. sheet.

Large quantities also find application in making lead chambers for the manufacture of sulphuric acid and for other purposes in chemical industry where resistance to corroding agents is required.

For the conveyance of water, lead piping has been used since Roman times. The Romans made it by rolling up sheet-lead, and there are definite instructions as to size and weight in the old Latin authors. A pipe 10 ft. long and 5 fingers in circumference weighed 60 lbs., and so on in proportion. The earliest of the Roman lead pipes are stamped with the name of the Emperor ; later ones have added to them the name of the officinator, under whose direction they were made, and sometimes, also, the name of the slave who made the pipe, the owner of the house in which it was laid, and the capacity of the pipe.

The modern method of making lead pipes is by "squirting," or forcing the metal under high pressure through a mould. The lead container is a cylinder open above and fitting tightly into a hollow ram, the aperture of which is supplied with an adjustable die. A stout rod or mandrel, firmly fixed to the bottom of the cylinder, stands upright and projects into the die, an annular space separating the two. The cylinder is filled with molten lead and after this has consolidated, and while still hot, the cylinder is forced upwards by hydraulic pressure. The lead is thus forced through the annular space between the mandrel and the die, and the length of the piping produced is only limited by the capacity of the container and the thickness and diameter of the piping ; the latter can be varied by selection of die and mandrel.

Lead is one of the heaviest of the common metals, its specific gravity being 11·34. The expression so often heard, "as heavy as lead" is well justified in view of the frequent use of the metal in circumstances where weight and compactness are desired ; as in window-weights, plummets, leads for sounding, etc. A racing yacht may carry 60–70 tons of lead on its keel as a counterpoise to its lofty sails. On the other hand, the specific gravity of lead only slightly exceeds that of silver (10·75) and is considerably less than that of many other metals, *e.g.*, mercury, 13·6; gold, 19·3; platinum, 21·5; and the rare metal osmium is, bulk for bulk, almost twice as heavy as lead, its specific gravity being 22·5.

The specific gravity of molten lead is 10·64,[1] notably less than the solid. Unlike water, then, when lead freezes the solid crystals sink in the liquid metal, and it will be remembered that in pattinsonising, the crystals of pure lead are fished out from the bottom of the bath. The handling of large quantities of lead in practice involves much labour which can often be avoided, as in transferring from the softening furnace to the zincing pots, by syphoning the molten metal. For that purpose, an iron pipe slightly bent is used, and care must be taken that the depth of the bath and height of syphon are such that the barometric column of molten lead is not exceeded. If the mercury barometer stands at 30 ins., then the height of the lead barometer will be

$$30 \text{ ins.} \times \frac{\text{S.G. of mercury}}{\text{S.G. of lead}} = 30 \times \frac{13{\cdot}6}{10{\cdot}6} = 38{\cdot}5 \text{ ins.}$$

It will, therefore, be impossible to syphon lead when the height of the syphon above the level of lead in the bath exceeds 38·5 ins.

The melting point of lead is 327° C., notably higher than tin, but lower than many common metals such as iron, copper, zinc, and gold. It is said to boil at about 1500° C.; certainly it shows decided volatility under furnace conditions, and cases are on record where it has been completely dispersed on smelting, passing into the flues and bag-houses as fume. The volatility is greatly increased in presence of air, owing to the formation of oxide. Baths of molten lead are often used for attaining a constant high temperature, as in file-hardening and tempering of steel-springs.

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[1] One cubic foot of lead weighs 710 lbs. when solid ; 664 lbs. when molten.

The bluish-grey colour and high lustre of freshly-cut lead quickly disappear in air owing to superficial oxidation of the metal. The oxide combines with carbon dioxide forming a carbonate of lead which then is fairly resistant to atmospheric action. The artistic effect of the whitish patina produced in this way is extremely effective, especially in the case of leaded church steeples —" white as washed marble," as Lamb says of the spire of Harrow Church. When lead is finely divided, a large surface is exposed to the oxidising action of air, and the heat generated by the chemical action is sufficient to raise the metal to the temperature of ignition, with the result that the metal inflames. When lead tartrate is heated out of contact with air, the metal is left, mixed with charcoal, in a state of extremely fine division, and when sprinkled in air takes fire for the reason just given. This finely powdered metal is termed a lead pyrophorus.

Lead is also attacked by air dissolved in water, a fact of great importance since lead pipes are almost universally used for distributing drinking water, and lead, when taken into the system even in minute quantities over a long period acts as a powerful poison. It is fortunate, in this regard, that drinking waters contain certain salts, carbonates especially, which precipitate lead solutions, so that the lead becomes coated with an insoluble compound which preserves it from further attack. Nevertheless, conditions may arise which favour the dissolution of lead in drinking water, and lead pipes lined with tin or copper, provided they are properly made and carefully soldered, form an excellent safeguard against the risks of poisoning.

The softness of lead makes it an excellent material for modelling, and many objects of great artistic and architectural value are fashioned from the metal. Roman art of this kind was almost restricted to coffins, and these were used for the burial of important persons during the middle ages. Unfortunately, these coffins are liable to burst and corrode, and the condition of many crypts became so bad that the practice of burying in them had to be stopped. Cases for the preservation of the hearts of heroes and other distinguished people were also made of lead. A more cheerful aspect of the artistic use of lead is concerned with the making of statues and vases and pots for garden decoration, many fine examples of which are to be met with in this country.

The association of lead with the malignant planet Saturn has already been touched upon, and the evil symbolism of the metal is curiously illustrated by the ancient custom of inscribing curses and maledictions upon a sheet of the metal and burying this along with some personal and intimate belongings, such as nail-parings, of the person against whom the ill-will was felt. One tablet of this character which has been found expresses the wish " That nothinge maye prosper nor goe forwarde that Raufe Scrope take in hand."

An amusing and assuredly unique use of sheet-lead is gravely described by Pliny in his great *Natural History*. The translation runs as follows: " The emperor Nero, for so the gods willed it, could never sing to the full pitch of his voice, unless he had a plate of lead upon his chest."

Of other uses of the metal, more practical if less fanciful, mention may be made of the sheathing of cables, the filling of copper cylinders with lead in order to bend them, the manufacture of accumulators for storing electric energy, and of shot and bullets for sporting and warlike purposes. Accumulators are made of numbers of lead plates coated with oxide of lead, the whole being immersed in sulphuric acid. In charging, certain chemical changes take place, electrical energy being transformed into chemical energy, and the reversal of these changes during discharging is accompanied by the conversion of chemical into electrical energy, the whole system returning to its original state and allowing of the almost endless repetition of these processes.

Lead plays a great part in warfare, probably second among the metals to iron. Shrapnel bullets are made of lead, hardened by the addition of antimony—about 12·5 per cent. They are cast in iron moulds split in the middle or are cut from wire and trimmed mechanically.

An interesting method of making lead shot is described by Hooke in his *Micrographia* (1665). The metal in the form of fine filings is stratified in a crucible with quicklime powder and the crucible heated just high enough to melt the metal. Under these conditions, each filing, on melting, takes up the spherical form that small drops assume. "After washing the lime dust in fair water, all these small filings of the metal will subside to the bottom in a most curious powder, consisting all of exactly round globules, which, if it be fine, is excellent to make hour-glasses of."

The modern method of making shot is equally ingenious. The lead is alloyed with a small quantity of arsenic, which has the effect of increasing its mobility when molten, the liquid alloy poured through a colander and allowed to drop 100 to 200 ft. into water. The fine streams of metal break up into drops and these, falling freely under gravity, become spherical under the play of surface tension. The shot are collected from the tub, dried and sorted, and polished in a revolving drum with a little graphite. One method used to eliminate imperfectly formed shot is to allow them to roll down a sloping board. Those which are perfect attain the maximum velocity and shoot well over the end of the board into a separate gutter ; the imperfect shot do not travel so far and falling short of the gutter are gathered apart. Shot towers are often prominent objects owing to their height. Occasionally, old pit shafts are used in place of them.

Bullets for smooth-bore, small arms are hardened with antimony in order to give them greater penetrating power. Rifle bullets, on the other hand, are made of soft lead in order that they may take the grooves of the rifle, and the iron projectiles used in rifled ordnance, after being dipped in zinc, are coated with lead for the same purpose.

Alloys of Lead. Many metals when melted together form homogeneous mixtures which are termed alloys. Such mixtures may comprise two metals (binary alloys), three metals (ternary), or even more, and as the number of metals available is large and the proportion of each used is capable of considerable variation, it will be realised that it is possible to prepare an enormous number of alloys even of two metals, and still more, of course, when three or more metals are used. The constitution of a solid alloy may also be very complex and may vary in alloys of the same metals according to the relative proportions of the metals present. A silver-lead alloy, for example, which contains less than 2·5 per cent. of silver, yields first on cooling crystals of pure lead, and these continue to grow from a liquor growing steadily richer in silver until the liquor attains the eutectic composition. When this happens, the liquor freezes as an intimate mixture of lead and silver crystals.

Again, a silver-lead alloy containing more than 2·5 per cent. of silver would first deposit crystals of pure silver, the liquor becoming progressively poorer in silver until again the eutectic composition was reached. Thus in these examples the solid alloy would consist of fairly large crystals of lead and silver respectively, embedded in a fine-grained eutectic in each case. When it is remembered that these relationships vary enormously for every mixture of metals, that, in addition, some pairs of metals form chemical compounds having very different properties from those of their components, it will be realised that the properties of metals can be greatly modified by alloying with other metals, and it will not be surprising that so many alloys are employed in the arts and manufactures, and indeed in everyday life.

It will be sufficient here to mention only a few of the chief alloys of lead. The hardening of lead by antimony has already been noted, and one of the main objects of lead softening is to effect the removal of the antimony. Hard lead has, however, properties which make it of great use in practice, and it is prepared either by alloying soft lead and antimony (the latter being derived by smelting antimony ores) or by smelting the antimonial scums from the lead softening process. Antimonial lead containing from 10–12 per cent. of antimony is used for making acid cocks, plugs, valves and injectors. Various forms of type metal also contain antimony, sometimes tin in addition, the best proportions being 76 parts of lead to 24 parts of antimony. Other compositions used for type metal are—

Lead.	Antimony.	Tin.
50	25	25
60	30	10

The necessary qualities of these alloys are that they should fill the moulds sharply, be easily cast, not be so soft that they bend and not so hard as to cut paper.

The alloys of lead and tin are widely used as pewter and solder. As pewter comes in contact with food and drink, it is necessary that the lead content should be kept low in order to avoid the risk of poisoning. English pewter contains 20 per cent. of lead, French 18 per cent., the remainder being tin.

Solders generally contain 1 or 2 parts by weight of lead to 1 of tin, and the same proportions were used by the Romans who had acquired great skill in soldering. The aim of soldering is to join two metals by means of a more fusible alloy having similar properties (*e.g.*, hardness and malleability) to the metals joined. It is essential that the surfaces should be clean and air must be excluded during the process so that oxidation is prevented. This is attained by the use of zinc chloride and tallow, resin, or some similar flux.

Chinese " tea-lead " used for lining tea-boxes is also an alloy of lead and tin in the proportions 9 : 1. In more recent times English sheet-lead has been imported into China for use in packing tea.

Bearing-metals or antifriction alloys are composed largely of lead, along with antimony, tin, and sometimes copper and zinc. The composition of these varies very much, the best and most expensive being richest in tin. The commoner ones may contain up to 90 per cent. of lead. Such alloys must contain both hard and soft constituents, the hard to resist abrasion and to carry the load, the soft to supply the necessary plasticity and to secure adjustment.

By a suitable combination of the four low melting metals, lead, bismuth, tin and cadmium, a number of easily fusible alloys can be prepared which find application in dentistry, as solders, as safety-plugs for boilers and for taking impressions of coins and woodcuts. The following table gives the composition and melting point of some of the best known of these fusible alloys, and also the melting points of the constituent metals. As all of these alloys melt below 100° C., a ready explanation can be found of the old conjuring trick of the spoon melting in a cup of tea.

FUSIBLE ALLOYS.

Name of Alloy.	Lead.	Bismuth.	Tin.	Cadmium.	Melting Point of Alloy.
Newton	5	2	3	—	94·5° C.
Rose	1	2	1	—	93·75
Lichtenberg	3	5	2	—	91·6
Wood	2	4	1	1	71·0
Lipowitz	8	15	4	3	60·0
Melting point of the individual metals	325°	264°	230°	320°	

The Atomic Weight of Lead. To the chemist, the atomic weight of an element is one of its most important properties, for it represents the proportion by weight in which the element combines with some other element selected as standard, and in fact with all elements with which it enters into chemical reaction. Thus the whole of quantitative chemistry is intimately bound up with the question of atomic weights and every practical worker, whether on purely scientific lines, or in the laboratory of the assayer, the city analyst or the chemical works, bases his results eventually on atomic weights.

From the earliest days of scientific chemistry, therefore, constant investigation of this subject has been pursued and the work continues with unabated zeal, with the result that this characteristic constant has been determined with a very high degree of accuracy for most of the elements. From a philosophical point of view the standard of comparison should be hydrogen, the lightest of the elements, but in actual practice it is found more suitable to select oxygen (= 16) as standard, the ratio of oxygen to hydrogen being 16 : 1·008. On this basis, the atomic weight of lead is 207·19, so that, for example, in litharge, Pb O, 207·19 parts by weight of lead are combined with exactly 16 parts by weight of oxygen. It may be remarked that only eight out of somewhat more than eighty well-characterised elements have atomic weights exceeding 200, the highest being uranium with atomic weight 238·2.

Now in 1914 the very remarkable discovery was made that the lead separated from certain uranium ores, which are distinguished by their radio-activity, had a lower atomic weight than what might be called common lead, that is the lead ordinarily won by smelting galena and its associated lead ores. This fact seemed so contrary to past experience that the subject has been investigated with the greatest diligence by some of the most distinguished chemists in European countries and America, and it has been definitely established that (1) the atomic weight of common lead from the most diverse sources is constant ; and (2) that the lead derived from radio-active minerals (sometimes termed radio-active lead or uranium-lead) has a lower atomic weight than common lead. The specific gravities of the two leads vary in a similar manner, that of higher atomic weight having the greater specific gravity, but the quotient of atomic weight and specific gravity, termed the atomic volume, is the same in each case. The actual data are—

	Atomic Weight.	Specific Gravity.	Atomic Volume.
Common Lead . .	207·19	11·337	18·277
Uranium Lead . .	206·08	11·273	18·281

Perhaps the most arresting feature of the situation is that the two forms of lead, though differing considerably in these particulars, are absolutely alike in chemical behaviour and cannot be separated from each other.

The problem of the two leads is a very complex one and is intimately bound up with the great subject of radio-activity, the intimate association in nature of uranium, radium and helium, and the proved spontaneous liberation of helium from radium compounds. The most widely accepted hypothesis to account for these relationships is that the atoms of uranium suffer disintegration, yielding a great variety of unstable products, prominent among which is radium, along with the inert gas helium ; this process is attended by the liberation of vast quantities of energy, partly in the form of heat, partly as radiations, some of which are identical with the X-rays, and the end-products are helium and this peculiar form of lead.

The dream of the alchemist was to transmute lead into gold. The modern chemist has become witness of a series of phenomena whereby, apparently, radium, a metal infinitely more precious than gold, is transformed into base lead. He is, however, an observer only, for he is as powerless to influence these changes as was the alchemist to ennoble his base metal.

CHAPTER XII

COMPOUNDS OF LEAD—LITHARGE AND RED LEAD

SOME of the compounds which lead forms with other elements have already been mentioned in connection with the metallurgy of the metal. For the sake of reference, a list of the most important of these compounds will be given, along with the name or names by which they are known and their chemical formulae—

Lead Sulphide (Galena), $Pb S$.
Lead Monoxide (Litharge, Massicot), $Pb O$.
Lead Peroxide, $Pb O_2$.
Red Lead (Minium), $Pb_3 O_4$.
Lead Hydroxide, $Pb (OH)_2$.
Lead Carbonate (Cerussite), $Pb CO_3$.
Lead Chloride (Horn Lead), $Pb Cl_2$.
Lead Nitrate, $Pb (NO_3)_2$.
Lead Sulphate (Anglesite), $Pb SO_4$.
Lead Acetate (Sugar of Lead), $Pb (C_2 H_3 O_2)_2$.
Lead Chromate, $Pb Cr O_4$.

To these may be added what are known chemically as the basic carbonates of lead, compounds of the normal carbonate, $Pb CO_3$, and the hydroxide of lead, $Pb (OH)_2$. One or more of these basic carbonates is an essential constituent of the white lead of commerce. The basic chlorides, similarly composed, occur as minerals and have, in the past, been prepared on a large scale for utilisation as pigments.

Many of these compounds are practically insoluble in water, *e.g.*, the sulphide, the oxides, the carbonate, the sulphate and the chromate. The nitrate and the acetate are easily soluble. The chloride is fairly soluble in boiling water, but sparingly in cold water ; when the hot solution is allowed to cool, the lead chloride crystallises out in minute white needles, constituting the "silver shower" of the old authors. The iodide of lead, PbI_2, behaves in a similar manner, and the hot solution yields, on cooling, brilliant platelets of a golden yellow colour, formerly known as the "golden shower."

Many of the above compounds are white; the iodide and chromate are yellow, the sulphide black, the monoxide yellow to buff. The qualification of "lead" by colour epithets is in common use; thus we have "red lead," Pb_3O_4; "white lead," the basic carbonate; and "blue lead" is used to describe the metal itself. The peroxide of lead is often termed the puce-coloured oxide. It may be noted in this connection that "black lead" contains no lead, but is the name of a variety of carbon (graphite) resembling lead in the way it marks paper.

From the point of view of their use in the arts, the most important compounds of lead are litharge, PbO, red lead, Pb_3O_4, white lead and lead chromate; and it is to these that attention will be more particularly directed in the following pages. The position which these bodies occupy in the painting industry is a commanding one, and their preparation is carried out on a large scale.

Litharge. Litharge is the ordinary product of the drossing or oxidation of lead; and it is also formed when lead carbonate is heated, carbon dioxide being evolved in this case. It was known to the ancients under various names, slight variations of colour and texture, arising from different methods of preparation, misleading them as to the essential identity of their products. The name litharge (Gr. *Λιθάργυρος*) means the stone of silver and doubtless owes its origin to the behaviour of the two bodies, litharge and silver, on the cupellation hearth. Other names which have been used for it are lead ashes (scoria plumbi) and burnt lead (plumbum ustum). In more recent times, the term massicot has been applied to lead monoxide which has not been melted, the word litharge being reserved for the compound which has solidified from the molten condition. This distinction has now almost, if not entirely, passed out of use. In the trade, "flake litharge" is often used to describe lead oxide which has been melted and the term is an apt one since the litharge on solidification is readily broken up into a coarse flaky powder.

The oxidation of molten lead is an interesting phenomenon. An irridescent pellicle of oxide is formed on the surface of the metal and this, moving about with the blast, gives a very vivid and ever changing display of colours. The addition of a small quantity of tin, and of some other metals, prevents the development of the coloured scum until the added metal is all oxidised. In the cupellation of silver-lead alloy, the same appearances are met with and the end of the process is marked by the vanishing of the scum and the flashing-out of the mirror-like mass of molten silver.

Much litharge is produced in the cupellation process, and afterwards reduced by coal in a reverberatory furnace. It is also the object of special manufacture, either as an intermediary in the production of red lead and chrome yellow (lead chromate) ; or for glazing, glass-making, the preparation of storage batteries, and for use in the oil and rubber industries.

The principle of manufacture is simple, molten lead being exposed to air at a regulated temperature ; but in practice it is a somewhat delicate matter to obtain a product suitably free from unaltered lead, red lead, iron and grit, and minute quantities of such impurities are sufficient to condemn the material for many of the purposes to which it is put.

One method used in the preparation of litharge is oxidation of lead in a small reverberatory furnace. The oxide as it is formed is pushed back so as to expose the surface of the metal to the action of the air. After withdrawal of the compound it is ground and levigated. A much finer product is obtained by blowing air, by means of a steam injector, on to the surface of molten lead which is heated and agitated in a covered iron pan. The litharge dust and vapours pass upwards through a shaft and thence into fume-condensing chambers, and the dust which settles out is levigated, or calcined and sifted.

The colour of litharge varies, as already stated, according to the method of preparation. Some of the best is canary-yellow and this on trituration or compression acquires a brownish tinge. The compound melts about 900° C., and has a high specific gravity, 9·36. It is an oxidising agent, and transfers its oxygen readily to metals with which it may be in contact. Thus the softening of hard lead by atmospheric oxidation is greatly facilitated by the litharge, which, as it were, carries oxygen from the air to the metallic impurities to be drossed, lead being regenerated.

Litharge is also a strong base, dissolving in acids and forming salts of lead. Acetic acid, for example, is neutralised by litharge with production of a clear solution of lead acetate. Addition of a soluble chromate to this solution will then precipitate the insoluble lead chromate. This method is used in the preparation of lead chrome pigments.

An important aspect of the basicity of litharge is its combination with the acidic oxide silica, SiO_2. When heated with this oxide, or with silicates of other metals, litharge forms an easily fusible silicate of lead, which, on cooling, sets to an impermeable glass-like substance.

Thus when sprinkled over heated earthenware, a surface glaze of lead silicate is formed which renders the article suitable for use with liquids. Fused with sand and potash, a mixture of silicates of lead and potassium is produced and this constitutes flint-glass. Similarly, lead monoxide and boric acid yield the lead borate-glass of very special properties which was used by Faraday in his optical investigations.

One result of the ease with which molten litharge combines with silica is that it exercises a very corrosive action on the brickwork and such materials used in building furnaces. In softening furnaces the pans are made of iron, and in cupellation furnaces, where large quantities of highly heated litharge are formed, the hearth material (bone ash, marl, etc.), is selected especially to withstand this corrosive action.

Red Lead or Minium. The red lead of commerce is a body of somewhat varying composition, containing always a considerable amount of an oxide of lead having the formula Pb_3O_4. Comparison of this formula with that of litharge, PbO, indicates a higher stage of oxidation of lead, and this is reflected in the methods used in the preparation of these two oxides. In practice, red lead is produced from metallic lead *via* the monoxide, and this, the first product of oxidation, is converted into red lead by further oxidation with air.

The process thus falls naturally into two stages; the drossing stage, in which massicot is formed; and the colouring stage in which the massicot is converted into red lead. The furnaces used are built like a baker's oven. On each side is a fire-place, separated from the hearth by a low wall or fire-bridge, and the hot gases striking the roof of the oven heat the charge by radiation, without actually coming in contact with the metal or the oxide. The hearth is small, slopes towards the middle and front, and is closed in front by a working door. For ease in rabbling, a hook is suspended in front of the oven and this serves as a rest for the tools employed in the operation. Over the furnace-door is a hood through which poisonous fumes, issuing from the furnace, escape. Both drossing and colouring are often carried out in the same furnace; sometimes the more delicate operation of colouring is performed in a muffle furnace, so that contact of the oxide with furnace gases is avoided.

In the drossing process, several hundredweights of lead are melted on the hearth and a dam of coarse litharge and lead from the washing of a previous charge is built across the front, so that a pool of liquid lead is maintained. The working door is kept open and the lead freely exposed to air, the temperature being kept so low (about 340°) that the oxide formed is not melted. As the quantity of oxide increases, it is pushed towards the back of the furnace with a long-handled rake and the drossing is continued for twenty-four hours. At the end of this period, the dam is breached and the unaltered lead run off into moulds; the litharge is withdrawn from the furnace into iron wagons, allowed to cool, then ground with water and the finer material collected in settling vats. The coarse lumps of litharge along with some unaltered lead are gathered apart and used to build the dam for subsequent drossing operations.

In the colouring process, the fine mud of litharge from the settling vats is placed in the oven and exposed freely to air at a carefully regulated temperature, which is somewhat higher than that used in drossing. The charge is stirred and turned over to promote contact with air, and samples are withdrawn at intervals in order that the progress of colouring may be observed. When the correct tint has been acquired, the red lead is removed and may be ground if necessary. The time occupied in colouring is about forty-eight hours.

Orange mineral is a commercial form of red lead, differing, as its name indicates, in colour and also in other details, though essentially the same in composition. It is prepared from white lead which is treated similarly to the litharge in the colouring process just described. On heating white lead it readily loses carbon dioxide and water, which escape in the gaseous condition, and leaves a residue of lead monoxide. This is then capable of oxidation to orange lead and in fact comports itself just like the oxide prepared from lead.

It is of interest to note that orange lead is stated by Pliny to have been discovered accidentally by the burning of a house, in which were some jars containing white lead. Pliny's term for red lead, "cerussa usta," or burnt white lead, expresses this relationship between the two bodies. Minium was originally the name given to cinnabar or mercuric sulphide, but as this was so often adulterated with red lead, the term minium became applied in time to the adulterant. Minium was used as a paint three centuries before the Christian era, and the word *minio* meant "I paint in red lead." From the word is derived the English "miniature," which, with the progress of time, has lost entirely all association with red lead.

When used for glass-making, it is essential that red lead should be free, or practically so, from copper and iron, both of which impart colours to glass. Red lead is largely used as a pigment ; to a less extent in the manufacture of electric accumulators and as a jointing paste. When heated, it darkens in colour, becoming violet and then black, and the original colour is regained on cooling. At a higher temperature, oxygen is evolved and a residue of litharge is obtained.

CHAPTER XIII

WHITE LEAD AND OTHER LEAD PIGMENTS

THIS, the most important derivative of lead, has been known since the times when Greece and Rome occupied the premier positions among the nations. Many of the classical authors give recipes for the preparation of white lead and mention its extensive use in painting, and to some extent as a cosmetic. By the Greeks it was known as "psimythion," by the Romans as "cerussa," and it is from the latter word that the name "ceruse," once commonly used in England, is derived.

The manufacture of white lead is an industry of great importance at the present day, and much of the enormous output of lead is applied to the making of this pigment. Some statistics for the year 1912 will illustrate this. (*v.* C. A. Klein. *The Oil and Colour Trades Journal*, 1913. 6th December.)

In this year, the production of pig lead was 1,100,000 tons, and of white lead, 275,000 tons. Over 96 per cent. of the white lead was manufactured in six countries, the quantities being as follows—

United States	120,000	tons.
England	55,000	,,
Germany	36,000	,,
France	23,000	,,
Belgium	15,000	,,
Russia	14,500	,,

The remaining 10,000 tons was made in Italy, Holland, Spain, and Canada.

By far the greater quantity of this white lead was made by the Stack or Dutch process (180,000 tons);

the Chamber process was responsible for 45,000 tons, and 50,000 tons were produced in various other ways. Some of these processes will be described presently.

White lead, like red lead, is not a preparation of definite composition, but there is a general consensus of opinion that it is essentially a basic carbonate of lead, of the formula $Pb(OH)_2\,2\,PbCO_3$, otherwise written $3\,PbO,\ 2\,CO_2,\ H_2O$, probably always containing some normal carbonate of lead, $PbCO_3$, and other basic carbonates. It will suffice for our purpose to represent white lead, as above, by the formula $3\,PbO,\ 2\,CO_2,\ H_2O$, as this symbolism facilitates some chemical considerations we shall have to make on the subject.

It must be remembered that this formula indicates a chemical compound, with definite properties differing from those of its constituents. White lead does not contain litharge PbO, as such, or carbon dioxide, CO_2, or water, H_2O (nor, if the other formula be preferred, does it necessarily contain free $Pb(OH)_2$ or free $PbCO_3$), but may be regarded as the resultant of the chemical interaction of all three, each losing, as is commonly the case in chemical union, its specific properties. By heating white lead, this union can be dissolved, chemical change sets in and, with progressive rise of temperature, water and carbon dioxide are set free and litharge remains.

The question might be asked whether it is possible to re-unite water, carbon dioxide and litharge (or lead and oxygen which combine readily to form litharge) and thus be able to make white lead direct from these simple materials ? Under certain conditions this is possible, even on a manufacturing scale, but for long ages, the intervention of acetic acid was necessary, and even to-day this acid is very largely used as an intermediary, so to speak, in the preparation of white lead, and is essential both in the stack and chamber process, by which most of the pigment is made.

The stack process is undoubtedly the lineal descendant of the oldest methods of the Greeks and Romans. The recipes of these peoples mention lead and vinegar and sometimes fermenting materials, in which the vessels were embedded, in order that a gentle heat, necessary for the reactions to take place, might be maintained. Of the generation of carbon dioxide from the fermenting matter and the absorption of atmospheric oxygen from the permeating air, the ancients knew nothing. The Venetians, and later the Dutch, who excelled in the manufacture of white lead, used horse-dung and stable litter as sources of heat and carbon dioxide, and this was supplanted in 1787 by spent tan bark, the material still used in the stacks.

The Stack Process. For making white lead by the stack or Dutch process, the materials required are lead, vinegar, spent tan bark, moisture and air. The lead should be pure and contain, in particular, very little copper and silver. The desilverised metal usually possesses the requisite properties ; it may be further softened before use.

Vinegar is a dilute solution of acetic acid, $H_4 C_2 O_2$, prepared by the oxidation of ordinary alcohol, such oxidation taking place when alcoholic liquors become sour. It is also prepared by distilling wood. Very weak solutions, about 3 per cent., are used in the white lead process. Acetic acid, like all acids, neutralises bases forming salts. Lead oxide, $Pb O$, or lead hydroxide, $Pb (OH)_2$ react with acetic acid and the salt lead acetate, $Pb (C_2 H_3 O_2)_2$, and water are the products of reaction. Lead acetate can combine with either oxide or hydroxide of lead and yields thereby basic acetates.

Normal and basic acetates of lead play an important part in the manufacture of white lead.

Spent tan bark has a two-fold function in the process. By its fermentation carbon dioxide is produced, and this becomes bound, as it were, in the white lead. In addition, the complex chemical reactions of fermentation generate heat, just as they do in a hay-stack or in any accumulation of vegetable matter, and this heat is necessary to carry on the specific chemical actions upon which the process is based.

There is no lack of moisture, both the bark and the acid solution containing large quantities of it. Oxygen is derived from the air which permeates or diffuses through the stack and for which, in some cases, provision is made by means of ventilators.

The chemical reactions taking place in the process are briefly as follows. Metallic lead becomes oxidised by atmospheric oxygen to lead monoxide which in presence of water forms the hydroxide, $Pb\,(OH)_2$. Lead hydroxide is then neutralised by acetic acid, yielding lead acetate, and this salt combines with lead hydroxide to form a basic lead acetate. By the action of carbon dioxide on the basic acetate, the basic carbonate of lead or white lead is produced and lead acetate is regenerated. This regenerated lead acetate is then available for reaction with more lead hydroxide, and thus the cycle of reactions is repeated. It follows from this that the acetic acid is used over and over again in the form of lead salt during the process, and consequently the amount consumed is small. It would be still smaller were it not that some escapes with the waste vapours, and some is retained as lead salt in the finished corrosions.

The actual process for corroding lead, that is converting it into white lead, is carried out in large brick chambers, access to which is gained by openings in the front which are boarded up during the building of the stack. The acetic acid is contained in stout earthenware pots, the lower part (or well) of which is glazed. About one pint of acid is used in each pot and there is ample room above the surface of the acid for placing coils or buckles of lead, and these are held in position and kept from direct contact with the acid by projections inside the pot. The lead for corroding is cast in the form of straps, long and narrow sheets of thin metal, or in circular buckles, with perforations. To build up the stack, a layer of tan bark is spread on the floor, trodden down, and the loaded pots placed side by side upon this. Straps of metal are laid across the tops of the pots and above this a cover of boards, which serve as the floor for another layer of tan, pots and lead. Proceeding in this way the stack is built about 12 layers high, the weight of lead set out in one stack being perhaps 100 tons.

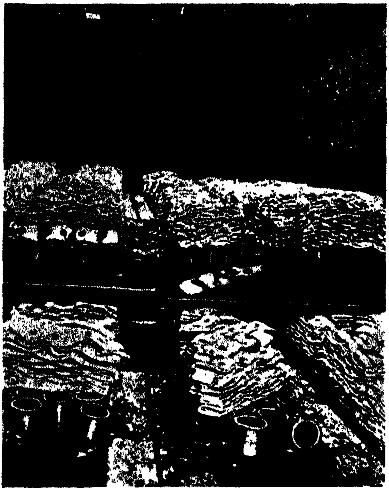

Fig. 15

MANUFACTURE OF WHITE LEAD BY THE STACK PROCESS

A partly dismantled stack showing the acid pots embedded in spent oak bark, the corrosions resting on the pots, and the method of building up the stack.

It is important that the tan should be in the right condition for fermentation, and it is customary to use about one-third of fresh tan each time, the remainder coming from dismantled stacks. Fermentation may be started by mixing a little horse-dung with the tan.

When the building of the stack is completed, the reactions sketched above set in and considerable volumes of steam and other gases escape from the top. After the lapse of a suitable interval of time (about 3 months), the stack is taken down, the layers being removed from the top downwards. The buckles or straps are then changed into a white porcelain-like material, usually having a core of unaltered metallic lead, and preserving their original shape, though thicker and laminated. These are collected, after being sprayed with water in order to keep down dust, and sent to the crushing and grinding mills.

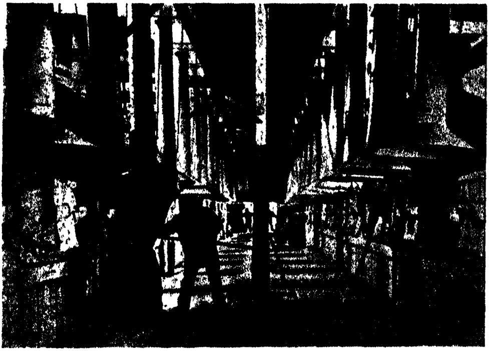

Fig. 16

DRYING WHITE LEAD

The wet cakes from the filter-presses are dried in water-heated pans. The photograph shows the elaborate arrangement of exhaust pipes and hoods connected with each drier for the purpose of carrying off the poisonous dust.

The corrosions are crushed between grooved rollers and screened, then passed through flattening rollers in order to flatten out particles of lead and put through finer sieves. A good deal of the unaltered blue lead is retained in this way, and the white lead which passes the screens is ground finely in stone mills and washed thoroughly with water in a series of washing and settling vessels. The corrosions as they come from the stacks contain lead acetate and the presence of this is detrimental to the finished pigment and must be removed by careful washing.

From the settling vats the white lead is removed in the form of a fine mud or paste to large pans heated with steam, where it is dried and then ground with oil to form a paint. Another method, now extensively used, is to grind the wet pulp directly with oil. During the grinding the oil and white lead become incorporated, and the water rises to the surface and is run off. This method, by the avoidance of the preparation and handling of dry white lead, is advantageous to the worker, who is preserved from coming in contact with the poisonous dust so easily raised from the dry powder.

The Chamber Process. The corrosion of lead by this process, though depending on the same chemical reactions, involves the use of very different appliances from those just described for the stack process, and some of the reacting substances are presented in different form. Carbon dioxide, instead of being generated by fermentation of tan bark, is produced by the combustion of coke; water is supplied in the form of vapour, and acetic acid, which in the pure condition is a liquid boiling at a slightly higher temperature than water, is volatilised and also comes into the chamber as a vapour. It is characteristic of this process that the carbon dioxide, water and acetic acid are all generated in suitable form and quantity outside the chamber in which the chemical reactions take place.

The chambers themselves are roomy brick buildings supplied with numerous wood bars over which the straps or thin sheets of cast lead are hung. Carbon dioxide and the vapours of water and acetic acid are prepared, as described above, beneath the chambers, and together with air pass into them through pipes in the floor. As these vapours are warm, they afford the necessary temperature at which they react with the lead. The excess of air, moisture and other vapours escape into the open at the top of the chamber.

By this arrangement, it is possible to exercise more control over the chemical reactions, the temperature, and the relative quantities of reacting bodies, than in the stack process, and, in addition, there is less risk of the white lead becoming discoloured, as it frequently does in the latter process, by admixture with bark or contamination with dark watery droppings from it. The time of reaction is also very greatly diminished.

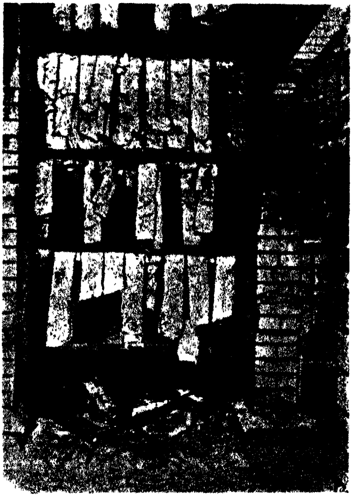

Fig. 17

MANUFACTURE OF WHITE LEAD BY THE CHAMBER PROCESS

Showing the corroded straps of lead hanging in the chamber. The gases necessary in the process enter through a pipe in the floor of the chamber.

When the reaction is over, the chamber is opened, the corrosions removed, after drenching with water in order to prevent dust from arising, and sent to the crushing and grinding mills, where they are treated exactly in the same manner as the corrosions from the stacks.

This method has been extensively used in Germany, and to a less extent in England, but has apparently not been so successful in America. About four times as much white lead is produced by the old stack method as by the chamber process.

The Mild or Rowley Process. The manufacture of white lead has constantly been the subject of experiment and invention, and many are the ingenious methods which have been proposed and tried, either to shorten the period of preparation in the old-established processes, or to produce the desired product from other materials. The value of a white lead depends to a large extent on its physical character, and many of the methods which yield a white lead similar in chemical composition to the stack or chamber-made article, fail in respect to the physical properties of the product. Thus despite the expenditure of much inventive energy, the older processes hold their own and many would-be improvements have failed to establish themselves.

It would serve no useful purpose to recount these unsuccessful methods, or even to describe those which have met only with a limited measure of success. One exception may, however, be made in the case of the mild process, since the chemical features of this are so attractive in their simplicity.

As the name somewhat vaguely indicates, there are no strong or corrosive chemical agents, like vinegar, used in this process; in fact, the materials are of the simplest conceivable, having regard to the composition of the white lead. They are lead, oxygen, water and carbon dioxide, and the problem is to bring about the successive chemical reactions which lead to the formation of the basic carbonate of lead. This is simply achieved by first oxidising the lead in presence of water and then carbonating (or treating with carbon dioxide) the hydrates of lead formed in the first stage.

For the oxidation and hydration of the lead a very finely divided metal is required. This is prepared by subjecting a thin stream of molten lead to a high pressure blast of superheated steam. The operation is carried out in a large steel chamber on the floor of which is water, a foot or two deep. The blast is directed downwards and blows the metal into a kind of mist which immediately solidifies on meeting the water, producing a metallic mud. This mud is withdrawn by mechanical means, fed into cylinders and agitated 24–36 hours by blowing a stream of air through. Oxidation and hydration of the lead take place, and the product consists of variously coloured hydrates of lead, of somewhat indefinite composition, but probably containing lead hydroxide $Pb(OH)_2$ and other hydroxides richer in lead.

Some 80–90 per cent. of the lead is hydrated at this stage and the hydrated mass is levigated to free it from unaltered lead, which is returned for fresh treatment. The hydrate is transferred to another set of cylinders, water added in sufficient amount and flue gases, carefully scrubbed to remove dust, and containing about 18 per cent. of carbon dioxide, are passed through. After a little time, vigorous reaction takes place, with great increase in bulk of the solid matter, carbon dioxide and water are absorbed and reacting chemically with the hydrate produce the required white lead. The carbonation process lasts for 36 hours. The white lead does not require grinding, being in the form of a very fine precipitate, nor is washing necessary since the liquors and the solid carry no impurities. After simple filtration, the white lead can be dried or ground with oil in the usual way.

Two outstanding advantages of this process, as compared with the stack and chamber process, are the freedom of the white lead from lead acetate and the absence of corrosions. All white lead prepared by means of acetic acid contains soluble lead acetate, the removal of which is essential, otherwise the value of the pigment is deteriorated, and this involves a lengthy washing process. The collection of the corrosions from stacks and chamber is again a laborious matter and one which may, unless suitable precautions are taken, be attended by the formation of poisonous dust. The corrosions, too, are hard and require careful crushing and grinding in order to remove the cores of blue lead and to get the white lead in a fine state of sub-division. In the mild process there is no handling of the material from the melting of the lead until the finished product is obtained.

Other Pigments Containing Lead. Lead compounds are the basis of many valuable pigments, some of which are white and, being alleged to be non-poisonous, have been proposed as substitutes for white lead; while others, like the lead chromates, are coloured yellow, orange and red, and are prepared without particular reference to such considerations.

It is of interest to note that again the basic salts play an important part in these pigments, and in two cases, at least, the mineral galena has served as the raw material for their manufacture.

The chloride of lead, $PbCl_2$, is soluble in water, especially in hot water, and is unsuitable for use as a pigment, but the basic chloride, Pb OH Cl is insoluble, and used to be made commercially by precipitation of solution of chloride of lead with milk of lime. The chloride of lead was obtained by dissolving galena in hydrochloric acid. This process was invented by Pattinson and the product named after him, "Pattinson's White." Though now no longer in use, it deserves mention because of its chemical interest and of its association with the inventor of the famous desilverising process.

Lead sulphate, Pb SO_4, is very sparingly soluble in water, but does not possess other properties desirable for use as a pigment. What is often regarded as a basic sulphate is, however, made on a large scale directly from galena, and by a dry method. The galena is strongly heated in a furnace and a blast of air blown on to the surface of the mineral. The galena is volatilised and oxidised by the air, when in the form of vapour, to oxide and sulphate of lead, or possibly a compound of these, the basic sulphate. Any zinc ore that may be mixed with galena, and this is usually the case, is simultaneously oxidised to zinc oxide, itself a valuable pigment, and this, along with the basic sulphate of lead, passes off in the form of fume. This fume is collected in flues and bag-houses and comes into the market under the name of "Sublimed White Lead." Exception may be taken to the name, as the term white lead has come to connote a basic carbonate of lead, and its application to what is essentially a sulphate is misleading. This pigment is exceedingly fine-grained and is seldom worked up into a paint alone, but is valuable for mixing with other pigments. It is not so sensitive to blackening, owing to the formation of lead sulphide by reaction with hydrogen sulphide, as is white lead.

The lead chromates, as mentioned above, are coloured. They are produced very simply by mixing solutions of lead salts and chromates ; the lead chromates, being insoluble in water, are precipitated and only require to be washed and dried to fit them for use.

The source of the lead salt is litharge which is dissolved in a suitable acid, either acetic or nitric acid. Litharge used for the purpose must be free from red lead and grit which are insoluble in these acids. Into the dilute solution of the lead salt, a solution of chromate or bichromate of potassium or sodium is slowly run, under constant stirring, care being taken that the temperature is kept low.

By the addition of sodium sulphate along with the chromate solution, lead sulphate is precipitated simultaneously with lead chromate, and as the sulphate is white, a mixed pigment of lighter shade is obtained. To intensify the colour of the lead chromate it is digested with an alkali, caustic soda or milk of lime, the effect of which is to make the salt basic, and this is accompanied by a deepening of the tint.

By the adoption of such methods a variety of pigments is produced, *e.g.*, canary yellow, chrome yellow, chrome orange, lemon yellow, several thousand tons of which are made annually.

Paints. White lead and the other preparations of lead described in the foregoing pages are pigments, that is, insoluble colouring materials. To convert a pigment into a paint it is necessary that it should be thoroughly incorporated with a vehicle or medium which, in the case of an oil paint, is a drying oil like linseed oil. The drying of such an oil is a chemical process depending on the absorption of, and chemical reaction with, the oxygen of the air, and it is facilitated by boiling the oil, or by the addition of relatively small quantities of such materials as the oxides of lead or manganese. Dilution with turpentine also promotes drying. For practical working, a volatile solvent is also added in order that the working quality of the paint may be correctly adjusted. Thus the vehicle contains, in general, a drying oil and, in subsidiary amount, dryers and thinners.

The grinding of paints is a matter of great practical importance, but one into which space will not allow us to enter. Suffice it to say that much of the value of the paint depends on the thorough incorporation of pigment and vehicle. A paint has a two-fold service to render; it must be decorative in effect and it must preserve the object which it covers from the disintegration wrought by weathering agencies. The value of white lead in these respects is universally admitted. It has more covering power than any other single white pigment, and the paint has the practical advantage that it can be worked either stiff or thin. It is invaluable for outdoor work, but is liable to blackening indoors owing to attack by hydrogen sulphide.

CHAPTER XIV

LEAD IN MEDICINE AND LEAD POISONING

MANY lead preparations are used in medicine. That striking figure of the sixteenth century, Paracelsus, who was largely responsible for diverting the chemists of his age from the pursuit of transmutation into the more practical fields of preparing medicines, used to boast that he could cure 200 diseases by means of lead preparations. It was remarked, however, by van Helmont, a century later, that Paracelsus did not tell of the many hundreds he had killed by the same medicines.

Externally applied, lead compounds act as astringents and local sedatives and are used as lotions and ointments, frequently in conjunction with opium. Most plasters contain lead oleate, which is, chemically speaking, a lead soap and is prepared by boiling litharge with olive oil. The method of preparing this is almost identical with that described by Pliny nineteen centuries ago.

Great care must be exercised in using lead salts internally, for when concentrated they are powerful irritants. In small quantities and in dilute solution the acetate is employed as an astringent in diarrhoea and gastric ulcer. It is also used as a gargle.

Lead acetate has a sweet taste and is commonly known as sugar of lead. It is prepared by neutralising acetic acid with litharge. When wine turns sour, acetic acid is formed by the oxidation of alcohol. A method of sweetening sour wine by boiling it in leaden vessels or by addition of litharge has been known almost from the earliest times, and has been practised even in comparatively recent times. It is obvious that such methods would render the wine sweet, both by neutralisation of the acetic acid and by the addition of the sweet-tasting lead acetate.

Such is the danger to health involved in the practice, however, that it has long been forbidden in some countries and, at one period, even the death penalty was exacted for this offence in Germany. This form of sophistication was very prevalent in Paris even so late as the eighteenth century.

Lead arsenate is used as an insecticide in viniculture and horticulture. It is prepared by precipitation of the solution of a lead salt with an arsenate.

Mention may be made here of the use of white lead as a cosmetic. It was greatly favoured by the Roman ladies and its use has extended to other countries in more recent times. The incompatibility of white lead with hydrogen sulphide, which has already been commented on, is stated to have been strikingly demonstrated on more than one occasion when these painted ladies have sought the sulphur waters of fashionable spas.

The poisonous character of lead compounds has long been recognised. "Lead colic" was described by Hippocrates in the fifth century B.C., and some centuries later by Vitruvius and Pliny. In more recent times "metallic colic," "lead distemper" and "mill reek" have been traced to the fumes produced in lead smelting; the "dry bellyache" which attacked the soldiers in Jamaica was found by Hunter to be due to the drinking of rum contaminated with lead, and other cases of illness from drinking wines have been proved to be caused by the action of the wine (presumably sour) upon the lead glaze of the vessels in which it was stored.

The extensive use of lead piping for the conveyance of drinking water has frequently given rise to lead poisoning, and there are so many articles containing lead in common use that people in the most varied occupations in life often fall victims to the complaint. Among great painters, for example, it is stated that Correggio, Raphael and Michael Angelo suffered from lead poisoning. But it is among those engaged in smelting, in the manufacture of white lead and other compounds of lead, and in those classes of artisans who use these things, plumbers, coach painters, pottery makers, etc., that the incidence is heaviest.

Writing of the manufacture of white lead, Vernatti, in 1678, describes the symptoms of poisoning, often attending the operation, in these words: "Immediate pain in the guts, and costiveness that yields not to cathartícks, hardly to often repeated clysters: best to lenitives, oil of olives, or strong new wort. Next, a vertigo, or dizziness in the head, with continual great pains in the brows, blindness, stupidity, and paralytick affections, loss of appetite, sickness, and frequent vomitings."

These symptoms evidently refer to sudden and violent attacks. The earlier stages of less rapid poisoning are marked by pallor and anaemia. With the development of the complaint a characteristic blue line appears along the margin of the gums near the teeth. This is not a universal symptom, but seems to depend on a septic condition of the mouth, since it rarely occurs in the case of people with sound teeth and clean gums. Another common feature of the complaint is the "wrist drop," caused by paralysis of the muscles of the fingers. Despite these marked symptoms, the diagnosis of lead poisoning is not always an easy matter, and at least one case is on record of a man, certified to be suffering from plumbism, who worked in a factory where only zinc white was used.

There is considerable variation in the susceptibility of individuals to poisoning by lead. Women are twice or thrice as susceptible as men; dark people less than fair; Italians less than English. Malnutrition, syphilis, gout, and alcoholism, as might be expected, lessen the resistance of the system. The investigations of the last few decades have established the fact that the chief agency of poisoning is dust, and thus the lungs are the most important organ whereby the poison gains access to the body. Gastro-intestinal absorption is quite secondary and cutaneous absorption a very small factor.

Legislative measures to protect the workers in lead have been enacted in most, if not all, countries in which the industry exists. In England, the White Lead Commission was appointed in 1898, and various factory and workshop acts have been passed, both before, and after that date. Since 1895 it has been compulsory to notify cases of poisoning to the Chief Inspector of Factories. Safeguards for the workers in the form of exhaust ventilation to remove dust, and the provision of respirators, overalls, head coverings, baths and lavatories, along with scrupulous cleanliness, medical inspection, etc., have done much to mitigate the evil in factories where lead compounds are made or extensively used. Between 1900 and 1909 the number of poisoning cases showed a drop of nearly 48 per cent.

In trades where these special provisions do not apply, or where the conditions of work are such that safety measures cannot so readily be enforced, the decrease of plumbism is not so satisfactory and, indeed, the data may show an increase. In the following table, taken from Legge and Goadby's *Lead Poisoning and Lead Absorption* (1912), are given the statistics for lead poisoning for the year 1911 in the various trades. Proportionately to the numbers employed, the tinning of metals appears as the most dangerous trade in that year, and next in order come the making of accumulators, vitreous enamelling, and white lead manufacture, the rate of attack per thousand being respectively 34, 28, 22 and 22.

CASES OF LEAD POISONING NOTIFIED FOR THE YEAR 1911.

Industry.	Total Number of Cases.	Fatal Cases.
Smelting of Metals	48	3
Brass Works	9	1
Sheet-lead and Lead Piping	12	4
Plumbing and Soldering	37	2
Printing	32	2
File-cutting	18	2
Tinning of Metals	13	0
Vitreous Enamelling	19	1
White Lead	41	2
Red Lead	13	1
China and Earthenware	92	6
Litho-transfers	1	1
Glass Cutting and Polishing	5	0
Electric Accumulators	24	1
Paints and Colours	21	0
Coach and Car Painting	104	5
Ship-building	36	6
Use of Paint in other Industries	56	1
Other Industries	8	0

In the manufacture of white lead, the patient and skilful study of the problem and the provision of safeguards, especially in the form of exhaust ventilation in connection with all processes in which dust may arise (*v.* Fig. 16), has been attended with striking results. In 1899, the number of cases of lead poisoning among white lead workers was 399; in 1912, the number had decreased to less than 6 per cent. of this figure, viz., 23; and in 1918, not a single case of poisoning was recorded.

Though hardly a case of poisoning by lead, there is an interesting record in the *Philosophical Transactions* of 1756 of a man who died by swallowing molten lead. The mishap took place at the burning of the Eddystone Lighthouse in 1755, and the victim was Henry Hall, aged 94 years, " of a good constitution and extremely active for one of his age." Hall was reaching up in order to put out the flames when the lead from the lanthorn melted and some of the liquid metal, the temperature of which must have exceeded the melting point, namely, 325° C., ran over his face and down his throat. He survived the accident for twelve days, and after his death, a lump of metal 4 ins. long and 1½ ins. wide, weighing 11 ozs. 5 drs. 18 grs. was taken from his stomach, the inside of which was found to be rather badly burned.

Considering the ripe age of this victim, it would appear that the swallowing of molten lead is by no means so dangerous as one might have anticipated. The incident was sufficiently remarkable to induce some ill-advised person to seek confirmation by an experiment *in corpore vili.* Accordingly, three ounces of molten lead were poured down the throat of a cock. The unfortunate fowl did not appear greatly incommoded ; it pecked about for food as usual and when, after three days, it was killed, the stomach was opened and the lead removed in the presence of credible witnesses.

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